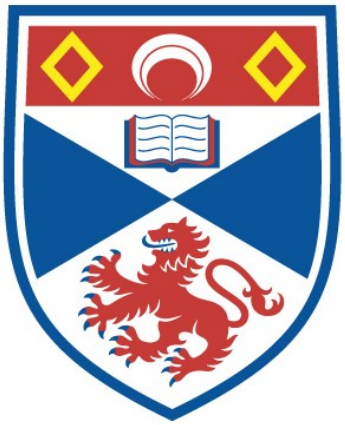
REACTIONS OF ACYLARYLNITROSAMINES

John Cook

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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REACTIONS OF ACYLARYLNITROSAMINES

A Thesis

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in the Faculty of Science of the

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by

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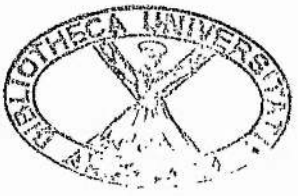


I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, University of St.Andrews and the Department of Chemistry, University of Edinburgh, under the supervision of Professor J.I.G. Cadogan since the 1st October 1967, the date of my admission as a research student.

I hereby certify that John Cook has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance No.16 (St.Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

ABSTRACT

The decomposition of acylarylnitrosamines in benzene and halogenomethanes has been studied. "Benzyne adducts" are formed in yields up to 82% in the decomposition of N-nitrosoacetanilide in the presence of various 2,3,4,5-tetraarylcyclopentadienones and anthracenes, and competition reactions using mixtures of arynophiles gave competition constants identical to those from similar reactions using authentic sources of benzyne. N-Nitrosoacetanilide did not, however react with furan to form 1,4-dihydronaphthalene-1,4-endoxide, and the yield of 1,2,3,4-tetraphenylnaphthalene formed in the reaction with 2,3,4,5-tetraphenylcyclopentadienone in benzene was gradually reduced from 22% to 1.4% on addition of furan. N-Nitrosoacetanilide has been shown to react with dimethylacetylenedicarboxylate in benzene to give cis-, and trans-dimethyl diphenylmaleates and 1,2,3,4-tetracarbomethoxynaphthalene in good yield, in addition to the expected biphenyl. The reaction of benzyne from pentyl nitrite and anthranilic acid, however, gave only 5,6,11,12-tetracarbomethoxydibenzo [a,e] cyclooctatetraene.

These results are discussed, and the suggestion

made that the intermediate leading to the formation of "aryne adducts" need not be a true aryne. An arynoid species, the dipolar conjugate base of the aryldiazonium cation, formed by removal of the o-proton, is suggested as a possible alternative.

The reactions of acylarylnitrosamines with halogenomethanes have also been studied, and the results compared with those of similar reactions of arylazotriphenylmethanes and aryldiazonium halides and fluoroborates. The participation of diazonium halides and acetate has been demonstrated in the reactions of N-nitrosoacetanilide, and possible mechanisms involving formation of diazonium halides have been suggested.

The decomposition of o-t-butyl-N-nitroso-acetanilide in halogenomethanes led to the formation of the o-, and m-t-butylphenyl halides, in addition to the o-, and m-t-butylphenyl acetates. Participation of 3-t-butylbenzyne was confirmed by the isolation of 5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide when o-t-butyl-N-nitrosoacetanilide was allowed to decompose in bromotrichloromethane in the presence of furan; this was accompanied by a suppression of formation of the m-t-butylphenyl halides and acetate. A reaction scheme is suggested involving participation

of diazonium halides and acetate.

The reaction of N-nitroso-N-formylanthranilic acid and N-nitroso-N-acetylanthranilic acid with 2,3,4,5-tetraphenylcyclopentadienone in benzene led to the formation of 1,2,3,4-tetraphenylnaphthalene, but the principal products in these reactions were 3,1-benzoxazin-4-one and 2-methyl-3,1-benzoxazin-4-one respectively.

ACKNOWLEDGEMENTS

I should like to express my thanks to Professor J.I.G.Cadogan for suggesting the topic of research, and to Professor Cadogan and Dr.J.T.Sharp for their continued advice and encouragement during the period in which the work was carried out.

In addition I wish to record my thanks to many members of the teaching, technical and secretarial staffs in the Department of Chemistry of both the University of St.Andrews and the University of Edinburgh for their assistance at various times.

Thanks are also due to the British Petroleum Company for samples of "galvinoxyl" and 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxide and to Dr.B.H.Klanderman of Eastman Kodak for samples of 1,4-dimethoxytriptycene and 5,12-dimethoxy-5,12-dihydro-5,12-ethenonaphthacene.

Finally I should like to thank the Science Research Council for the award of a Research Studentship for the period during which this work was carried out.

CONTENTS

INTRODUCTION

INTRODUCTION

The work described in this thesis concerns the mechanism of formation of aryne adducts from acylarylnitrosamines and the mechanism of the decomposition of the latter in halogenomethanes. In the former case, reactions were carried out in an aromatic solvent and the participation of arynes or arynoids, and free radicals was considered; while in the latter, the participation of aryl free radicals and aryldiazonium salts was considered.

The historical background to the development of these intermediates, and the relevance of their reactions in the elucidation of the mechanism of the decomposition of acylarylnitrosamines will now be discussed in a short review.

I ARYL RADICALS IN SOLUTION

A Historical outline

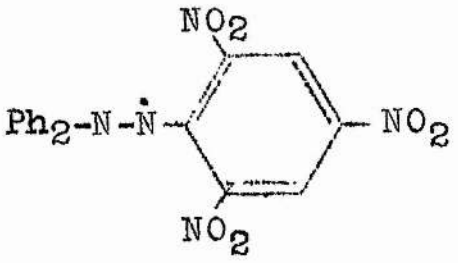
Evidence for the existence of "free radicals" first appeared in the chemical literature some 120 years ago with reports by Kolbe [1] and Frankland [2], (later proved to be erroneous) claiming the existence of free methyl and ethyl radicals, but it was not until 1900 when Gomberg [3], in attempting to synthesise hexaphenylethane, obtained instead the first true free radical, the triphenylmethyl radical. In 1929, Paneth and Hofeditz [4]

demonstrated the formation of methyl radicals in the gas phase by the pyrolysis of tetramethyl lead, and in elegant experiments were able to estimate their half-life as being of the order of 10^{-3} sec. As a result of these experiments, other radical reactions were recognised and identified. Thus in 1934, Backstrom [5] postulated aldehyde autoxidation as a free radical chain process, and Grieve and Hey [6] postulated the intermediacy of phenyl radicals in the decomposition of N-nitrosoacetanilide in aromatic solvents, while three years later, Hey and Waters [7] and Kharasch, Engelmann and Mayo [8] independently explained the anomalous formation of 1,3-dibromopropane from allyl bromide and hydrogen bromide in the presence of peroxides, by invoking a free radical chain mechanism. The large volume of work which followed these early milestones left no doubt that free radicals were intermediates in many chemical reactions.

B The nature of radicals

A radical may be defined as an atom or group of atoms with an unpaired electron, and it is to the ability of this free electron to form a strong electron-pair bond with a substrate that we attribute the great reactivity of radicals, Paneth and Hofeditz [4] demonstrated the short lifetime of radicals, but a short

lifetime need not be indicative of instability; thus while the acetoxy radical decomposes spontaneously to a methyl radical and carbon dioxide [9,10], many radicals e.g., methyl, phenyl, triphenylmethyl, are inherently stable, though not isolable as other than the dimer. (The dimer of the latter has recently been shown to have the methylene hexadiene, rather than the ethane structure [11]). Some free radicals on the other hand, e.g., diphenylpicrylhydrazyl (1) [12], "galvinoxyl" (2)[13], are stable, crystalline solids, and as a result of their resonance stabilisation and large steric hinderance to their combination, show little tendency to dimerise.



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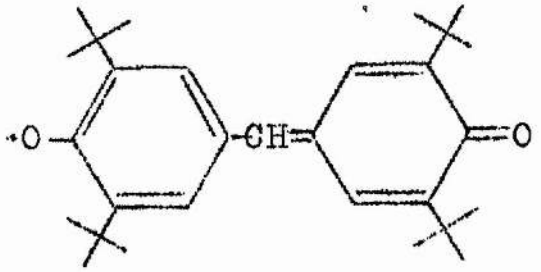


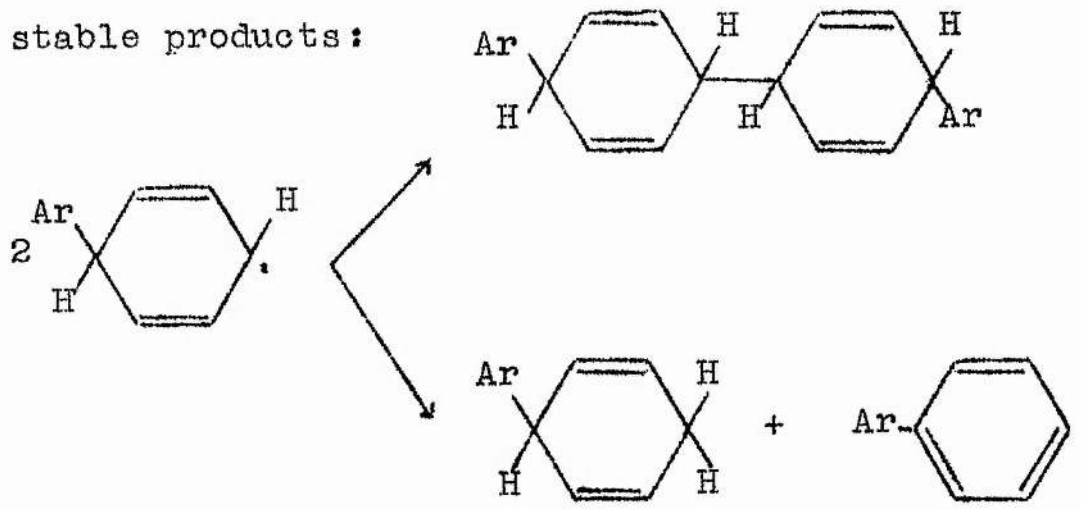
(2)

C Reactions of radicals in solution

As might be expected, the presence of unpaired electrons in free radicals is of overriding importance in determining their chemical properties, and the reactions of radicals occur in such a way as to reduce the instability associated with unpaired electrons.

Free radicals may dimerise or disproportionate as is demonstrated below where the arylcyclohexadienyl

radical [14,15], which possesses considerable resonance stabilisation, may react via two reaction schemes to give stable products:

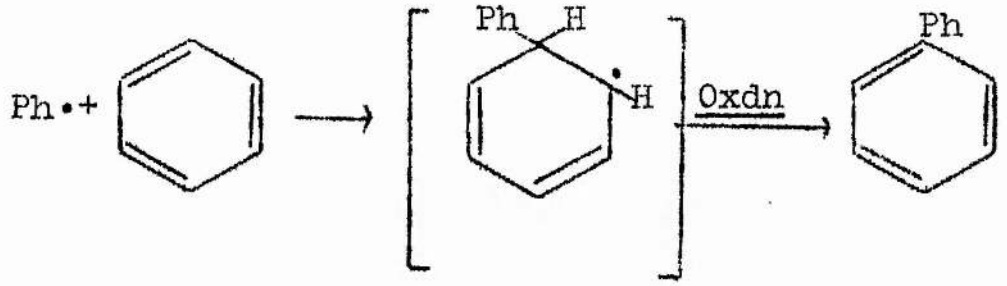


Abstraction reactions of aryl radicals were first studied by Boeseken and Gelissen [16,17], who obtained benzene and chlorobenzene respectively when dibenzoyl peroxide was allowed to decompose in chloroform and carbon tetrachloride.

$$(PhCO_2)_2 \longrightarrow PhCO_2\cdot \longrightarrow Ph\cdot \xrightarrow{CCl_4} PhCl + CCl_3\cdot$$

The abstraction reactions of radicals from various sources were later studied by Waters [18], Grieve and Hey [6], and Wieland [19] and were extended to other halogenomethanes and quantified by Hey and Peters [20], Cadogan, Hey and Hibbert [21,22] and Bridger and Russel [23]. The preferential abstraction of hydrogen to chlorine in chloroform was explained [20] by the differences in activation energies of the respective processes. Substitution reactions form the bulk of the reactions of aryl radicals; exemplified below by the homolytic aromatic substitution

of benzene; addition of a phenyl radical to the sub-



strate is followed by oxidation of the intermediate radical. As might be expected in view of the fact that aryl radicals are electrically neutral species, the reactions of radicals are characterised by an insensitivity to polar influences; thus the reactivities of various nuclei towards radical phenylation show little variation when compared to the large variation in reactivities towards nitration [24]:

Substrate	K_H^X (Ph•)	K_H^X (NO_2^+)
Benzene	1.0	1.0
Biphenyl	4.0	8.0
Nitrobenzene	2.9	1×10^{-6}
Chlorobenzene	1.4	0.033
Bromobenzene	1.7	0.03
Iodobenzene	1.8	0.18
Methyl benzoate	2.4	0.0037
Toluene	1.7	25
t-Butylbenzene	0.87	15.7

Again the complex kinetics exhibited by some reactions can only be satisfactorily explained in terms of radical intermediates; benzoyl peroxide, for example, has been shown to decompose in benzene by reactions, occurring simultaneously, of orders 1 and 1.5 [25,26].

The addition reactions of radicals have also been much studied; Kharasch [8] and Hey [7] and their co-workers explained the anomalous addition of hydrogen bromide to allyl bromide in the presence of peroxides on the basis of a free radical chain mechanism:

$$Br\cdot + Br\text{-}CH_2\text{-}CH{=}CH_2 \longrightarrow Br\text{-}CH_2\text{-}\dot{C}H\text{-}CH_2\text{-}Br$$

The free radical polymerisation of styrene has been shown to proceed via addition of phenyl radicals:

$$Ph\cdot + Ph\text{-}CH{=}CH_2 \longrightarrow Ph\text{-}\dot{C}H\text{-}CH_2\text{-}Ph$$

Fragmentation of radicals is shown by the unstable acetoxy radical which loses carbon dioxide to give the more stable methyl radical [9,10]:

$$CH_3CO_2\cdot \longrightarrow CH_3\cdot + CO_2$$

An allied reaction to the latter, but one of which few examples are known is the rearrangement of radicals:

e.g., [27]

$$Ph\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{-}CH_2\cdot \longrightarrow \cdot\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{-}CH_2Ph$$

In this rearrangement, the radical rearranges from one isomeric form to another in order to obtain an increase in resonance stabilisation.

D Sources of radicals in solution

Aryl radicals have been obtained at temperatures below 150° by thermolysis of covalent bonds, where the bond strength is not in excess of 40 kcal/mole. Hey [28] used the thermolysis of dibenzoyl peroxide and phenylazotriphenylmethane as sources of free radicals;

$$(PhCO_2)_2 \longrightarrow PhCO_2^{\bullet} \longrightarrow Ph^{\bullet} + CO_2$$

$$Ph\text{-}N{=}N\text{-}CPh_3 \longrightarrow Ph^{\bullet} + N_2 + CPh_3^{\bullet}$$

in the latter case verifying the work of Wieland, Popper and Seifried [29] who had shown spectroscopically that the thermolysis of phenylazotriphenylmethane gave phenyl and triphenylmethyl radicals as well as nitrogen. In reactions where dibenzoyl peroxide decomposed in an aromatic solvent, not all the benzoyloxy radicals fragmented directly to give phenyl radicals and carbon dioxide, for Hey [30] has shown that in addition, small quantities of benzoic acid and the isomeric aryl benzoates were formed.

Phenyl radicals are also formed in the thermolysis of lead tetrabenzoate [31], phenyliodosobenzoate [32], and silver halide dibenzoates [33]:

e.g., $(PhCO_2)_4Pb \longrightarrow 2PhCO_2^{\bullet} + Pb(CO_2Ph)_2$

$$\downarrow$$

$$2\,Ph^{\bullet} + 2CO_2$$

A similar reaction to the decomposition of phenylazo-

triphenylmethane is the reaction of 1-phenyl-3,3-dimethyltriazin [34] with hydrogen chloride in benzene:

$$Ph\text{-}N{=}N\text{-}NMe_2 + HCl \longrightarrow Ph\cdot + N_2 + \cdot NMe_2HCl$$

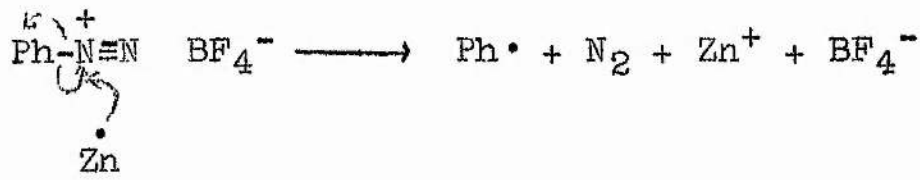
The Gomberg reaction [35] provided the first example of homolytic substitution, but the disadvantage of its being a heterogeneous reaction, and the production of much tarry material, reduced its synthetic value; the

$$PhN_2Cl + NaOH + PhH \longrightarrow Ph\text{-}Ph + N_2 + NaCl + H_2O$$

mechanism of this reaction will be discussed later. Waters [36] and Waring and Abrams [37], however, used instead, suspensions of the solid diazonium chloride as the source of phenyl radicals; which probably arise by homolysis of the covalent form of the salt with which the ionic form is in equilibrium:

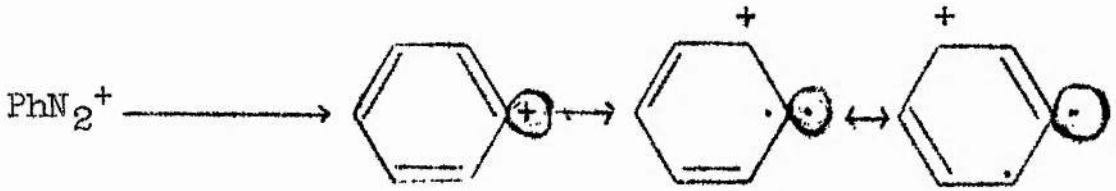
$$ArN_2^+\ Cl^- \rightleftharpoons Ar\text{-}N{=}N\text{-}Cl \longrightarrow Ar\cdot + N_2 + Cl\cdot$$

Benzenediazonium fluoroborate on the other hand, requires the presence of a catalyst such as zinc to facilitate formation of radicals via a one electron transfer process [38]:



Abramovitch [39] has shown that the purely thermal decomposition of benzenediazonium fluoroborate in an aromatic solvent gave mainly fluorobenzene along with a little

of the isomeric biaryls, but the isomer ratio of the latter did not agree with the intermediacy of an aryl radical and he suggested a radical ion intermediate:



and other canonical forms

In situ diazotisation [40] of the arylamine using pentyl nitrite is preferable in many cases, and although the mechanism has not been fully established, the aryl radicals probably arise by homolysis of the covalent diazoether:

$$ArNH_2 + C_5H_{11}ONO \longrightarrow Ar\text{-}N{=}N\text{-}OC_5H_{11} \longrightarrow Ar\cdot + N_2 + C_5H_{11}O\cdot$$

Photolysis of weak bonds has also been used successfully in the formation of phenyl radicals; thus diphenylmercury [41], tetraphenyl lead [41], triphenylbismuth [42] and iodobenzene[41], have all been shown to give free radicals upon photolysis.

Another important source of free aryl radicals which was much used by Hey and his co-workers, and the subject of this thesis, acylarylnitrosamines, will be discussed in detail in the next section.

II ACYLARYLNITROSAMINES

A Historical outline

Acylarylnitrosamines have been known for nearly a century now, for it was in 1876 that Fischer [43] first prepared N-nitrosoacetanilide by the nitrosation of acetanilide in acetic acid. Von Pechmann and Frobenius[44] observed that acetylation of benzenediazonium salt solutions gave the same compound, and suggested that an equilibrium existed between N-nitrosoacetanilide and benzene diazoacetate in solution:

$$PhN(NO)Ac \rightleftharpoons Ph\text{-}N{=}N\text{-}OAc$$

Bamberger [45] first utilised the reactions of these unstable compounds when he used the reaction of N-nitrosoacetanilide with benzene to prepare biphenyl, and it was this work, and the work of Kuhling [46] on

$$PhN(NO)Ac + PhH \longrightarrow Ph\text{-}Ph + N_2 + AcOH$$

the acetylation of diazonium compounds, which inspired the development of the Gomberg reaction in the 1920's. Gomberg [35] used the reaction of an alkaline diazonium salt solution with an aromatic substrate to prepare biaryls. The reaction mechanism, which has recently been rationalised by Ruchardt and Merz [47] in terms of a free radical chain process, will be discussed later. The reaction did not, however, achieve much success synthetically as the biaryl was formed in low yield along

with much tarry material. Grieve and Hey[6] later modified the reaction and allowed dry solutions of N-nitrosoacetanilide in a variety of aromatic solvents to decompose at room temperature. When N-nitrosoacetanilide reacted with toluene, chlorobenzene, nitrobenzene and benzaldehyde, 4-methylbiphenyl, 4-chlorobiphenyl, 4-nitrobiphenyl and biphenyl-4-aldehyde were formed; the same products as in the Gomberg reaction, but in higher yield. Grieve and Hey [6] noted the "amphoteric" nature (nucleophilic and electrophilic) of the common intermediate, and suggested that a free phenyl radical was involved in the decomposition. Although in these early experiments, generally, only the less soluble *para* isomer was isolated, it was later shown [28,48] that in the reactions of N-nitrosoacetanilide, (and those of phenylazotriphenylmethane and dibenzoyl peroxide) both *ortho* and *para* isomers (and in the case of reaction in ethyl benzoate, *meta* as well [28]) were formed. When more sophisticated separation techniques became available, it was shown that, in general, all positional isomers will be formed.

Measurement of the rate of evolution of nitrogen during the decomposition of N-nitrosoacetanilide in benzene, toluene, *m*-xylene, mesitylene, chlorobenzene, anisole and nitrobenzene were made by Hey[7,49] and

his collaborators, and it was shown that good first order plots were obtained in every case, and the value of the rate constant varied only slightly from one solvent to another. The same result was found when N-nitrosoacetanilide was allowed to decompose in carbon tetrachloride. Hey postulated a fast equilibrium process followed by a slow rate-determining homolysis of the diazoester to give phenyl and acetoxy radicals and nitrogen. Formation of acetic acid was postulated as being due to dimerisation of an acetoxy radical with a hydrogen atom.

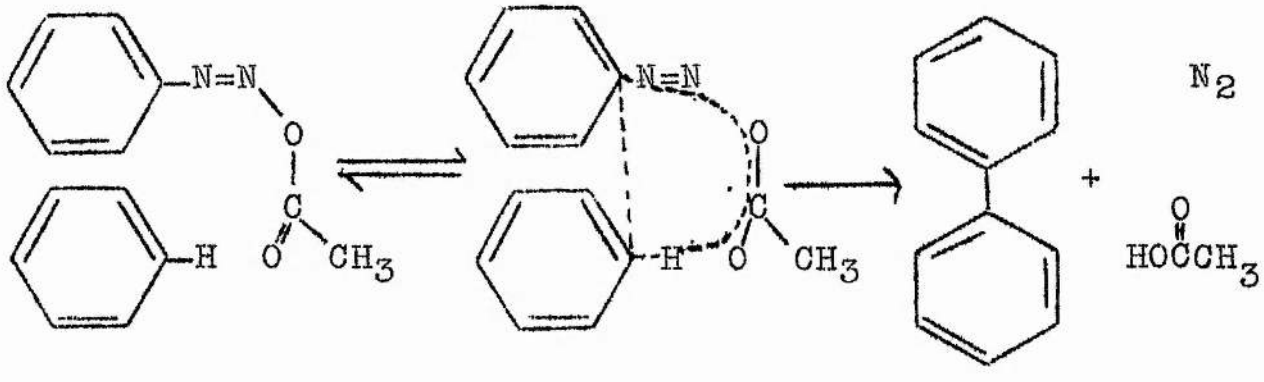
$$PhN(NO)Ac \overset{\text{fast}}{\rightleftharpoons} Ph\text{-}N{=}N\text{-}OAc \xrightarrow{\text{slow}} Ph\cdot + N_2 + AcO\cdot$$

$$Ph\cdot + C_6H_5R \longrightarrow p\text{-}Ph\text{-}C_6H_4\text{-}R + H\cdot$$

$$AcO\cdot + H\cdot \longrightarrow AcOH$$

The participation of acetoxy radicals was thought to be confirmed by the observation that small amounts of carbon dioxide were also formed in these reactions for it had been shown [36] earlier that acetoxy radicals decompose to methyl radicals and carbon dioxide. The participation of free phenyl radicals in the reactions of aromatic diazo compounds was questioned by Hodgson [50], who proposed elaborate ionic mechanisms for these reactions. Grieve and Hey [51] defended their theories of free radical phenylation, pointing out that Hodgson had used their theory in an attempt to

explain reactions to which it was not intended to apply. The unliklihood of the last step in Hey's scheme above, together with the knowledge that the polymers formed by the acylarylnitrosamine-initiated polymerisation of styrene, methyl methacrylate and acrylonitrile [52,53,54] gave little acyl group incorporation, led Huisgen and Horeld [55] to question the participation of free acetoxy radicals in the decomposition of N-nitrosoacetanilide. They suggested that instead of acetoxy radicals forming acetic acid, a concerted mechanism might be operative, where reaction of N-nitrosoacetanilide with benzene gave rise to simultaneous formation of biphenyl, nitrogen and acetic acid:



Huisgen and Horeld [55] also showed that N-nitrosoacetanilide coupled with 2-naphthol in a variety of solvents at 25° at the same rate as nitrogen was eliminated in the absence of 2-naphthol. They argued that the covalent diazoacetate must be the common intermediate

and that the rate-determining step was the rearrangement to the diazoacetate and not homolysis of the diazoacetate, as had been suggested by Butterworth and Hey [49]. They suggested the following mechanism:

$$PhN(NO)Ac \xrightarrow{slow} PhN{=}NOAc \xrightarrow[PhH]{fast} \text{biphenyl or azo coupling}$$

DeTar [56] extended this mechanism to account for results he obtained from the reaction in methanol. N-Nitrosoacetanilide in methanol gave formaldehyde, benzene, acetic acid and a little anisole. On adding sodium acetate, the yield of anisole dropped, but on adding sulphuric acid, anisole became the major product. De Tar reasoned that benzene was formed from phenyl radicals in neutral solution, but in acid solution, anisole must have resulted from the reaction with methanol of a phenyl carbonium ion and proposed:

$$PhN(NO)Ac \xrightarrow{slow} PhN{=}NOAc \xrightarrow{fast} Ph\cdot + N_2 + AcO\cdot$$

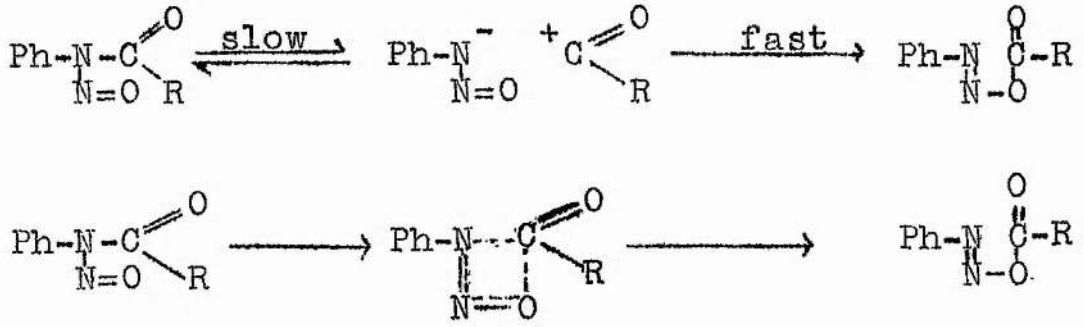
$$\Big\downarrow \text{very fast}$$

$$PhN_2^+ + AcO^- \xrightarrow{slow} Ph^+ + N_2$$

DeTar reasoned that the scheme accounts for the fall or increase in the amount of anisole formed on adding sodium acetate or sulphuric acid, since the former would tend to favour the diazoacetate in the equilibrium while addition of sulphuric acid would favour the diazonium ion. He also measured the amount of carbon dioxide formed in the reaction of N-nitroso-

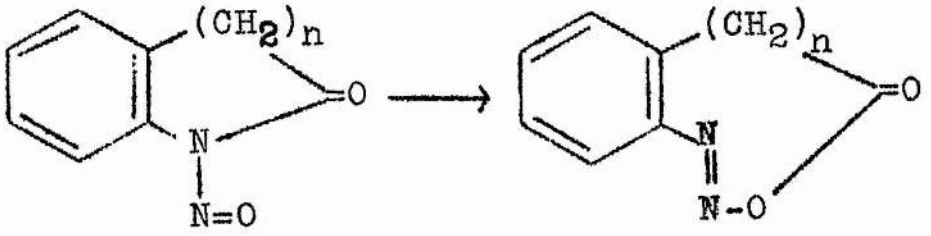
acetanilide with several solvents, and found that only in acetic anhydride was it appreciable (17.5%). He argued that acetoxy radicals have so short a lifetime that thereis insufficient time for them to decarboxylate except in acetic anhydride, towards which acetoxy radicals are less reactive. In acetic acid the major product was phenyl acetate (48%), which was thought to be formed in a purely ionic process, the equilibrium being largely in favour of the diazonium ion, which decomposed slowly to give molecular nitrogen and phenyl acetate.

The mechanism of the rearrangement of N-nitrosoacetanilide to the diazoacetate was elucidated during the early 1950's by the experiments of Hey [57] and Huisgen [58] both of whom considered the two possible schemes:



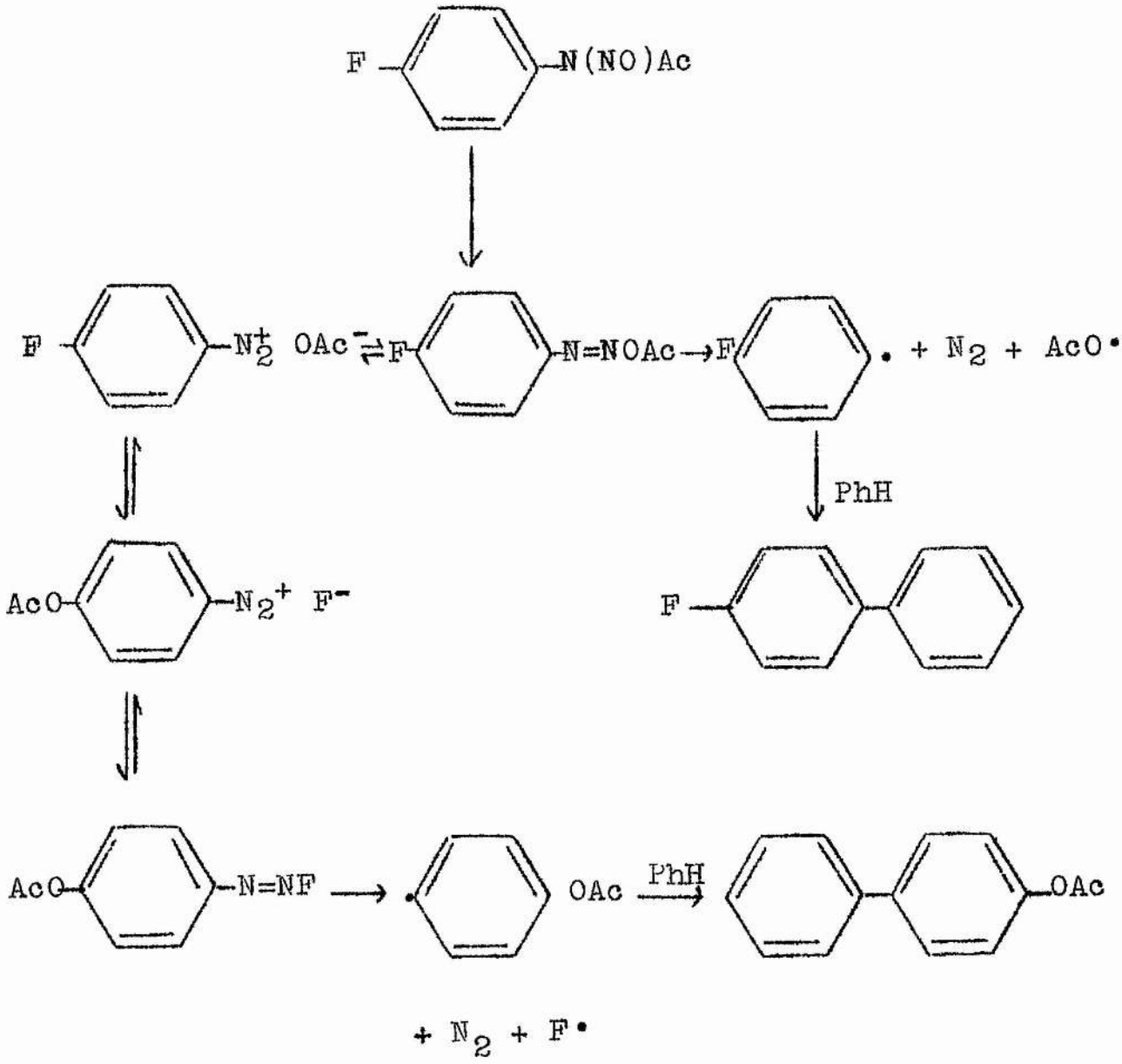
Consideration of, amongst other things, the effects of substituents [57,58(b)] on the rate of reaction led both teams to favour the non-ionic mechanism. That the intermediate diazoacetate had the trans rather than the cis configuration was demonstrated by Huisgen [58(d,e)] who showed that N-nitrosobenzolactams rearranged to

cyclic diazoesters only where n was greater or equal to



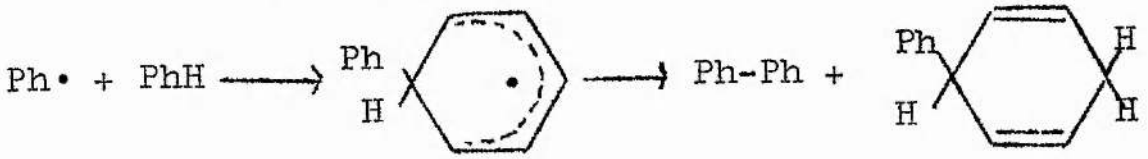
three, consistent with the product having the trans configuration.

In 1960 Suchitsky and his colleagues [59,60,61] investigated the decomposition of o-, and p-fluoro-N-nitrosoacetanilides and -benzanilides and found that 2-, and 4-acetoxybiphenyls were formed in addition to the expected 2-, and 4-fluorobiphenyls. m-Fluoro-N-nitrosoacetanilide, however, behaved normally. They rationalised this by postulating the formation of ion pairs from o-, and p-fluoro-N-nitrosoacetanilides and -benzanilides. Fluorine in the meta position, being less activated, would not be displaced (Scheme 1). The generality of ion pair formation was demonstrated by reacting p-fluoro-N-nitrosobenzanilide with various acetylarylnitrosamines, (p-H, CH_3, NO_2, Cl, m-CH_3) and in each case, the crossed product 4-acetoxybiphenyl was found. In 1962, Eliel and his colleagues [62] compared the reactions of phenylazotriphenylmethane on one hand, and N-nitrosoacetanilide on the other, and found that



Scheme 1.

in the latter, the expected dihydrobiphenyl, formed by disproportionation of the intermediate phenylcyclohexadienyl radical, was absent. They attributed this



to a "cage" reaction, where the phenyl and acetoxy

(or triphenylmethyl)radicals are generated simultaneously and in juxtaposition. Rapid reaction with the surrounding solvent cage would result in the simultaneous formation of biphenyl and acetic acid (or triphenylmethane). They later retracted [63] when indisputable evidence to the contrary was presented by other workers [64,65], and they themselves discovered that N-nitrosoacetanilide in benzene containing a low concentration of iodine afforded iodobenzene in high yield, thus indicating the presence of a truly "free radical".

Although the early free radical mechanisms for the decomposition of acylarylnitrosamines were successful in explaining the insensitivity of these reactions to polar factors, they were unable to explain the absence of quaterphenyls from the decomposition in benzene, and the absence of carbon dioxide which would result from fragmentation of the postulated intermediate acetoxy radicals. These early theories were therefore seen to require modification, and recent research results elucidating the mechanism of decomposition in aromatic solvents will be discussed below.

B Reactions with halogenomethanes

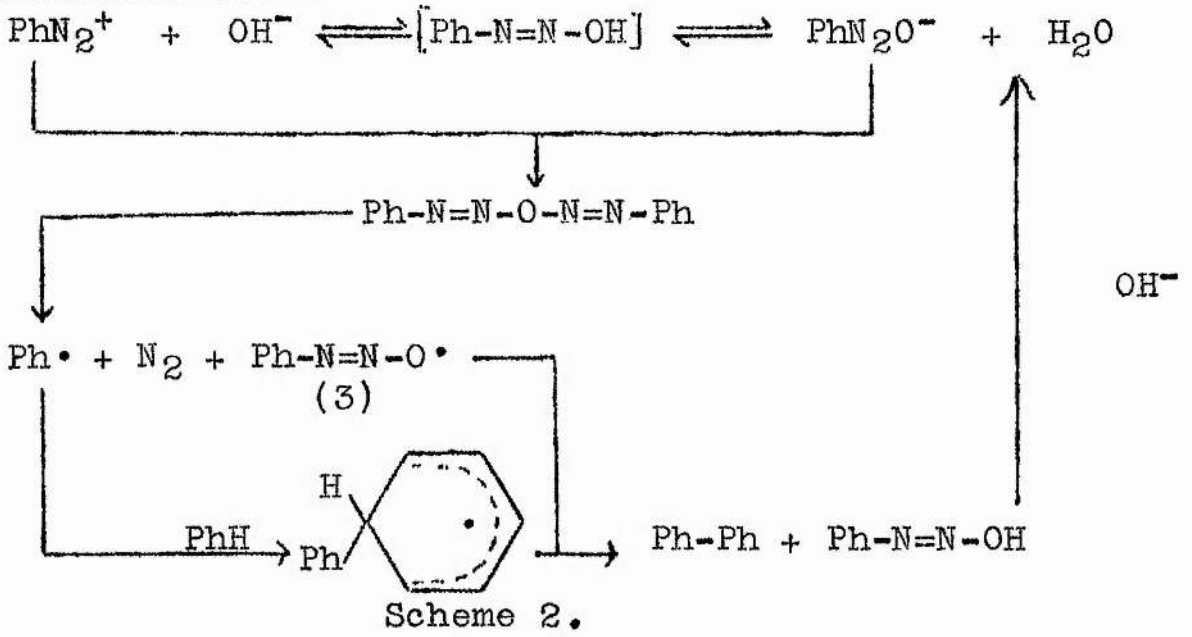
In 1934, Grieve and Hey [6] noted that N-nitrosoacetanilide in carbon tetrachloride gave chlorobenzene, nitrogen (50%) and precipitated benzenediazonium chloride.

This was confirmed by later workers [20,50] and hexachloroethane (the dimer of the trichloromethyl radicals) which is formed when dibenzoyl peroxide is used as the radical source [16], was found to be absent [20]. Whereas the phenyl radicals from dibenzoyl peroxide or phenylazotriphenylmethane abstract only hydrogen from chloroform, N-nitrosoacetanilide gave both benzene and chlorobenzene [20]. With bromoform, both benzene and bromobenzene were formed from all radical precursors [20,21,22] and bromotrichloromethane gave bromobenzene and chlorobenzene with N-nitrosoacetanilide, but negligible chlorine abstraction with other radical precursors. These surprising results and others recently obtained by Thomson [66] and Paton [67] will be further discussed in the Discussion in the light of the results of this present investigation.

C Recent results

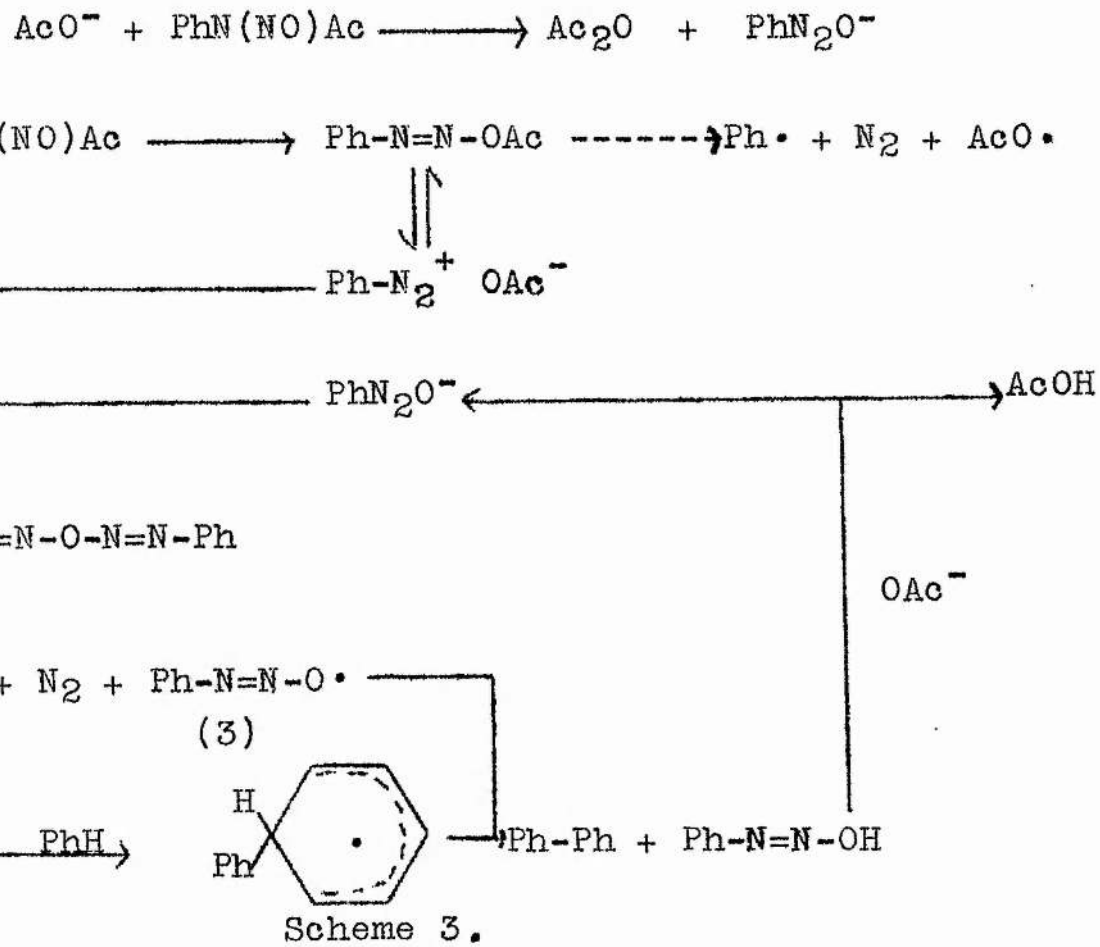
In 1964, Ruchardt and Merz [47] postulated a mechanism for the Gomberg reaction, in which aryl radicals were formed by the homolysis of an intermediate diazoanhydride (Scheme 2). Later that year, Ruchardt and Freudenberg [68] proposed a similar mechanism for the decomposition of N-nitrosoacetanilide in benzene (Scheme 3). It was postulated that phenyl

Ruchardt and Merz



Scheme 2.

Ruchardt and Freudenberg

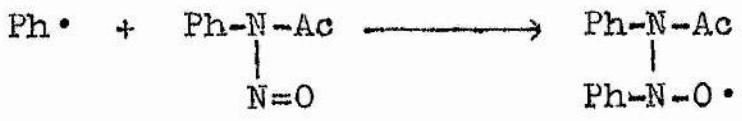


Scheme 3.

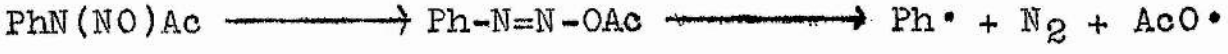
radicals were formed by homolysis of a diazoanhydride

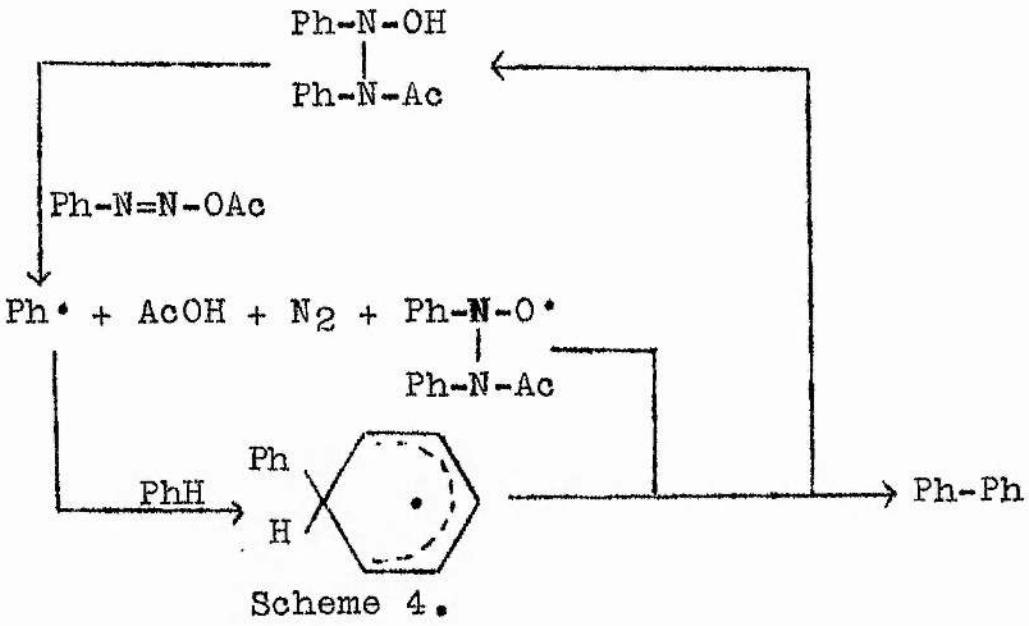
and that biphenyl and acetic acid were formed by a chain process with the diazotate radical (3) as chain carrier. Initial formation of the benzenediazotate ion was thought to be via attack of acetate on N-nitroso-acetanilide. Ruchardt and Freudenberg claimed that the high yield of acetic acid and the absence of carbon dioxide was explained by the intermediacy of acetate ions, not acetoxy radicals, and that the decomposition in acetic anhydride was by simple homolysis, reaction as above being prevented by reversal of the initiation step, which would be expected to give a high yield of carbon dioxide by fragmentation of acetoxy radicals. Ruchardt supported his mechanism by e.s.r. evidence [68,69] in which he claimed to have observed a signal which he attributed to the diazotate radical (3) when N-nitroso-acetanilide was allowed to decompose in the cavity of an e.s.r. spectrometer. Later results [70] clouded the issue, but in 1967 Hey and Perkins [71] suggested that the observed signal was not due to the diazotate radical but to a nitroxide radical, the (N-phenylacetamido)-phenyl nitroxide radical (PAPN) and suggested a modification of the Ruchardt mechanism with this radical (4) as chain carrier. Formation of the PAPN radical was seen as being by addition of a phenyl radical to N-nitrosoacetanilide (Scheme 4):

Perkins



(4)



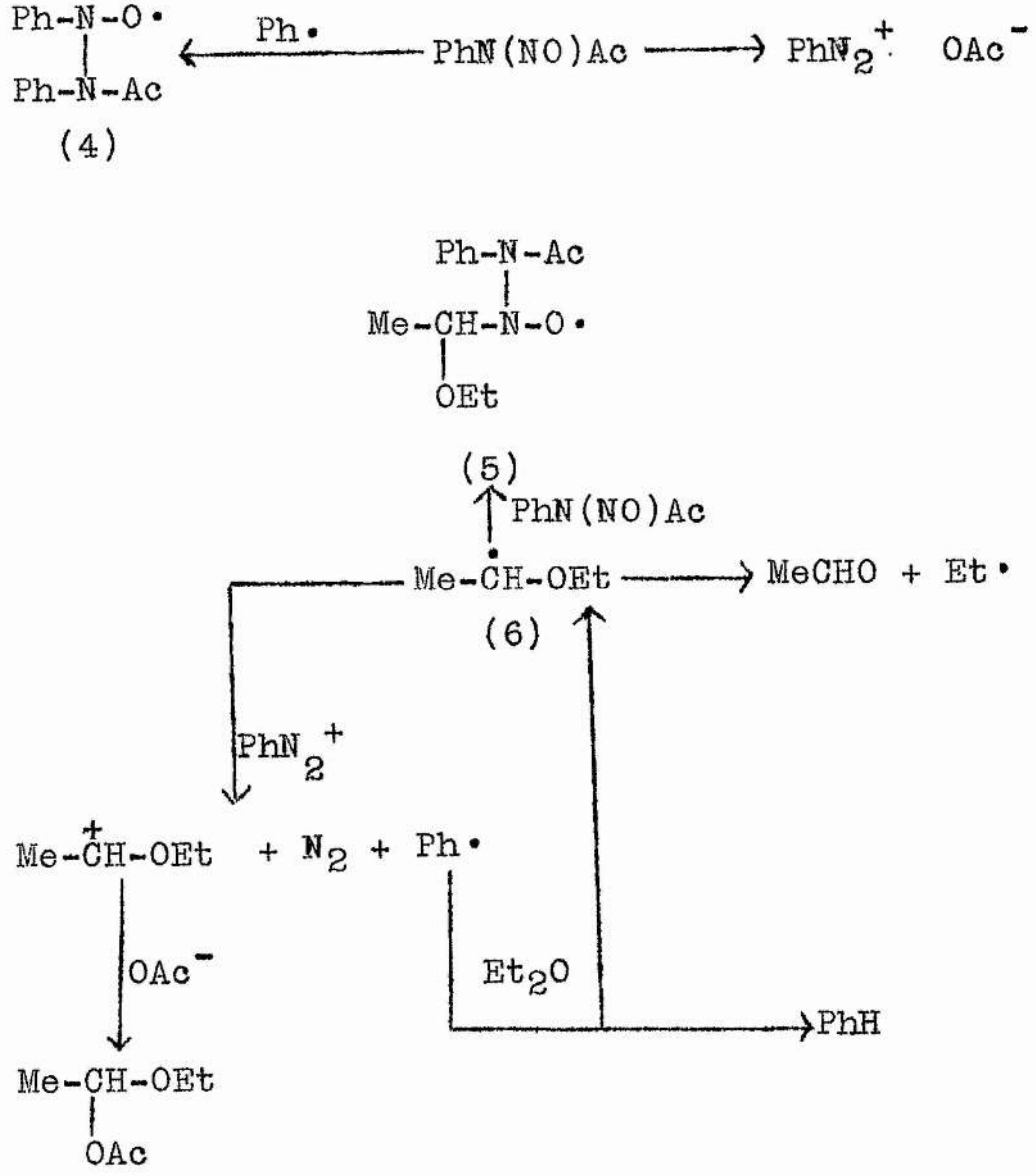


Scheme 4.

Chalfont and Perkins [72] synthesised the postulated intermediate radical (4) and showed that its e.s.r. signal was identical to that produced in the decomposition of N-nitrosoacetanilide. Two further independent syntheses confirmed the assignment [73]. In 1969, Cadogan, Paton and Thomson [74] showed that in the decomposition of N-nitrosoacetanilide in a variety of aromatic solvents, there was a second weaker e.s.r. signal which was almost obliterated by the signal due to the nitroxide radical in benzene, but was more easily

observable in solvents having an easily-abstractable hydrogen. This signal they attributedto the elusive diazotate radical (3), and supported their postulate with theoretical calculations on the closely-related σ-iminoxy radical (Ph-CH=N-O•). This would seem to support the Ruchardt rather than the Perkins scheme, (schemes 3 and 4) and Cadogan et al. have suggested that while reaction via scheme 4 cannot be ruled out, the diazotate radical is the significant chain-carrying radical and that the PAPN radical may be irrelevant to the production of phenyl radicals from N-nitrosoacetanilide.

In diethyl ether, N-nitrosoacetanilide has been shown by Denny [75] and his co-workers to give benzene (52%), 1-ethoxyethyl acetate (22%) and acetaldehyde (50%), but a fully satisfactory mechanism could not be advanced at that time. Cadogan, Paton and Thomson [76] have examined this reaction and e.s.r. studies revealed the existence of a new radical, to which they assigned the structure (5). The signal due to the diazotate radical was absent, and although a weak signal due to the PAPN radical was observed, the chain carrier was thought to be the phenyl radical, formed by a one electron transfer reaction between the diazonium cation and the α-ethoxyethyl radical (6). The resultant



Scheme 5.

α-ethoxyethyl carbonium ion was then scavenged by acetate ion to give the observed product (scheme 5).

The reactions of acylarylnitrosamines with carbon tetrachloride have recently been shown to proceed via a suspension of the diazonium carboxylate or chloride; Ruchardt and Tan [77,78] isolated benzenediazonium p-chlorobenzoate (84%) from the reaction of N-nitroso-

p-chlorobenzanilide with carbon tetrachloride at room temperature. The reaction of N-nitrosoacetanilide however, as had been shown earlier by Grieve and Hey [6], proceeded via a suspension of benzenediazonium chloride (20%). The significance of these results will be discussed in conjunction with the results of the present investigation in the Discussion.

D The question of aryne participation

The participation of arynes in the reactions of acylarylnitrosamines was first demonstrated by Cadogan and Hibbert [79] who showed that o-t-butyl-N-nitrosoacetanilide in benzene gave, instead of the expected o-t-butylbiphenyl, a mixture of the o-, and m-t-butylphenyl acetates in the ratio 2:1. This they attributed to the intermediacy of 3-t-butylbenzyne, and confirmed it by the isolation of 1-t-butyltriptycene when the reaction was done in the presence of anthracene. This exceptional behaviour was attributed to the steric effect of the bulky o-t-butyl group, which led to a suppression of phenylation, in favour of aryne formation. p-t-Butyl-N-nitrosoacetanilide on the other hand, not being sterically hindered, formed p-t-butylbiphenyl. However, Cadogan and his colleagues later showed [66,80,81] that the formation of aryne adducts from acylarylnitrosamines was not

confined to o-t-butyl-N-nitrosoacetanilide, for it was shown that other acylarylnitrosamines, including N-nitroso-acetanilide itself, in both benzene and carbon tetrachloride, gave aryne adducts with 2,3,4,5-tetraphenylcyclopentadienone, anthracene and 1,3-diphenylisobenzofuran. Indeed, even in the absence of an aryne trap, hydrogen abstraction from the acylarylnitrosamine was still observed; for N-nitroso-p-chlorobenzanilide in carbon tetrachloride gave p-chlorobenzoic acid as a primary product. Thus the premise that the large o-t-butyl group in o-t-butyl-N-nitrosoacetanilide alone was responsible for the manifestation of aryne behaviour was seen to require modification. Several other points emerged from these investigations:

(i) The yield of aryne adduct from a particular acylarylnitrosamine is the same in benzene and carbon tetrachloride, suggesting a common mechanism in the two solvents.

(ii) The yield of 1,2,3,4-tetraphenylnaphthalene depends on the nature of the acyl group, but is not simply related to the base strength of the acylate anion.

(iii) An acylarylnitrosamine with an electron-attracting ortho substituent in the anilino moiety does not form an adduct with 2,3,4,5-tetraphenyl-

cyclopentadienone.

(iv) An acylarylnitrosamine with a para substituent in the anilino moiety gives a lower yield of adduct than the corresponding unsubstituted compound.

(v) A meta substituent in the anilino moiety exerting a -I effect causes the formation of only one adduct, that corresponding to the 3- substituted benzyne.

(vi) A meta substituent in the anilino moiety exerting a +I effect, causes the formation of both adducts.

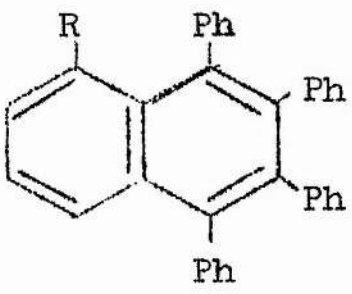
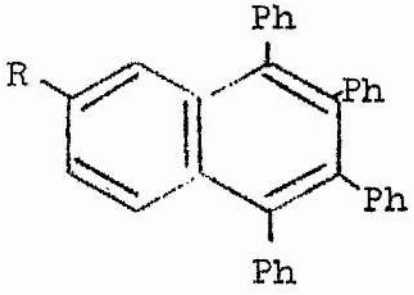
(vii) 1,2,3,4-Tetraphenylnaphthalene is not formed from reaction in furan or pyridine; tetrahydrofuran, however, behaved normally.

(viii) The presence of trace amounts of water drastically reduces the amount of adduct formed.

Benzyne adducts formed in the reactions of ArN(NO)COR

R in PhN(NO)COR	Solvent	Yield of T.P.N.(m/100m)
Me	Benzene	25
Me	Carbon tet.	21
Me	Furan	0
Me	Pyridine	0
Me	T.H.F.	24

Benzyne adducts formed in the reactions of $RC_6H_4N(NO)COC_6H_4Cl$

R	Solvent	Yield (m/100m) 	
o-Br	Benzene	0	-
m-Br	Carbon tet.	70	0
m-Br	Benzene	73	0
p-Br	Carbon tet.	-	4
m-Me	Carbon tet.	21	12
p-Me	Carbon tet.	-	1

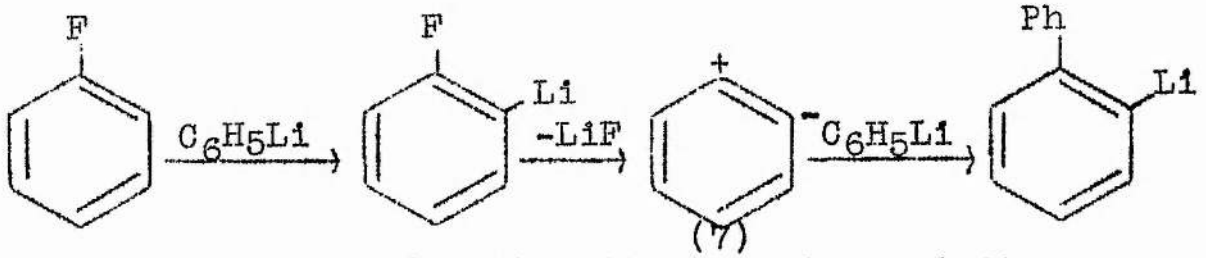
It is noteworthy also that in the reactions of N-nitroso-benzanilides, benzoic anhydrides, previously unreported products, were formed, thus providing evidence for the participation of a reaction such as the first step of the Ruchardt mechanism (scheme 3).

The reactions of arynes are discussed in the next section.

III ARYNES

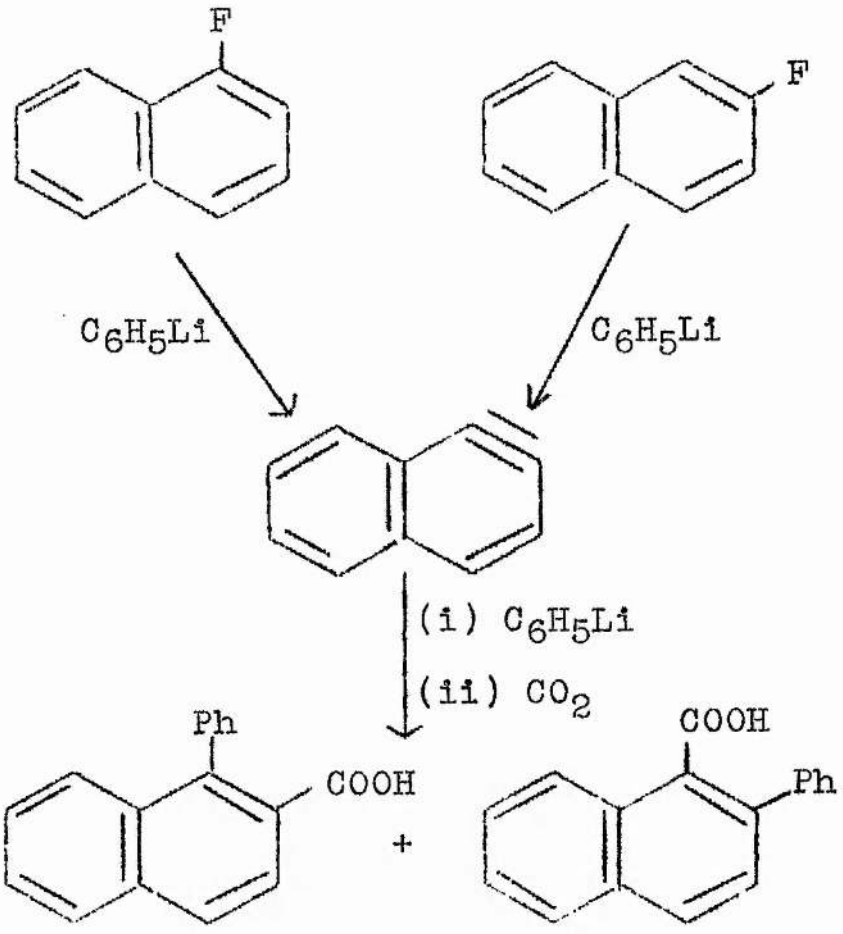
A Reactions of Arynes

A benzyne (C_6H_4) intermediate was postulated [82] as early as 1870 to explain the formation of biphenyl during the pyrolysis of diphenylmercury, but it was formulated in a manner which is no longer acceptable today, and it was not until 1942 that Wittig [83], in interpreting the experimental observation [84] that phenyl-lithium reacted with fluorobenzene to give biphenyl much faster than with any other halogenobenzene, successfully rationalised the situation. Wittig showed that 2-lithiobiphenyl, not biphenyl, was in fact the primary product, and accounted for its formation as follows:

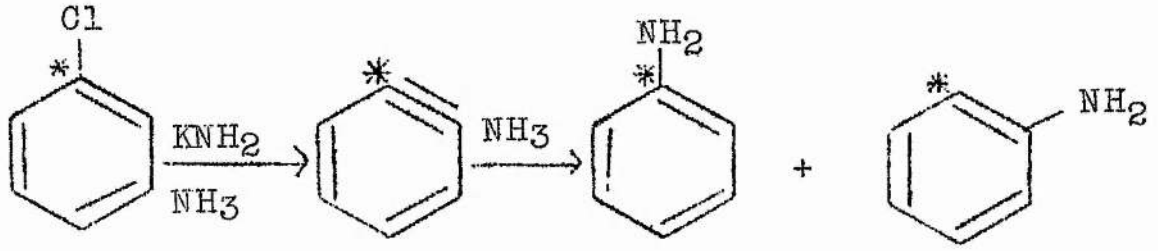


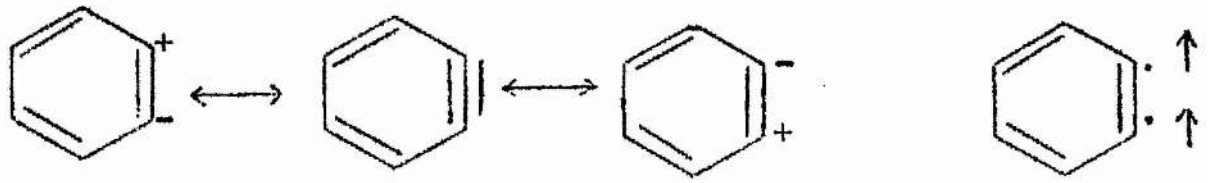
(7)

This scheme is in conformity with the high acidity of the ortho hydrogens in fluorobenzene. Wittig's original formulation of benzyne (7) as a permanently polarised species was seen to require modification when Huisgen and Rist [85,86] showed that the reaction of 1- and 2-fluoronaphthalene with phenyl-lithium, followed by reaction with carbon dioxide, gave the



same ratio of 1- and 2-phenylnaphthoic acids. Similarly, Roberts [87] and his colleagues obtained equal amounts of two differt isotopically-labelled anilines from the reaction of $[1\text{-}^{14}C]$ chlorobenzene with potassamide in liquid ammonia. Wittig now believes that the structure of benzyne in solution may be best represent-





(8)

ed as a resonance form of the three possible singlet structures; the possibility of the existence of the diradical triplet form (8) was discounted. Recent work [89] has confirmed the singlet structure, and shown that of the two possible singlet configurations, benzyne has the symmetrical singlet structure:

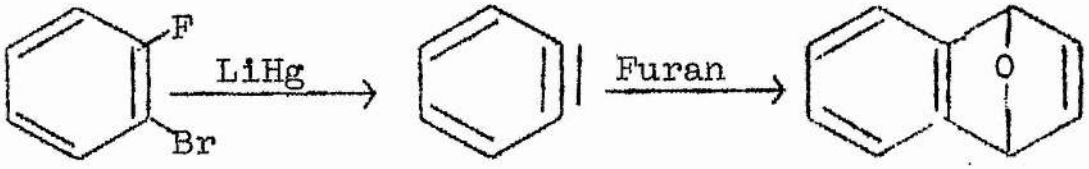
symmetrical singlet

antisymmetrical singlet

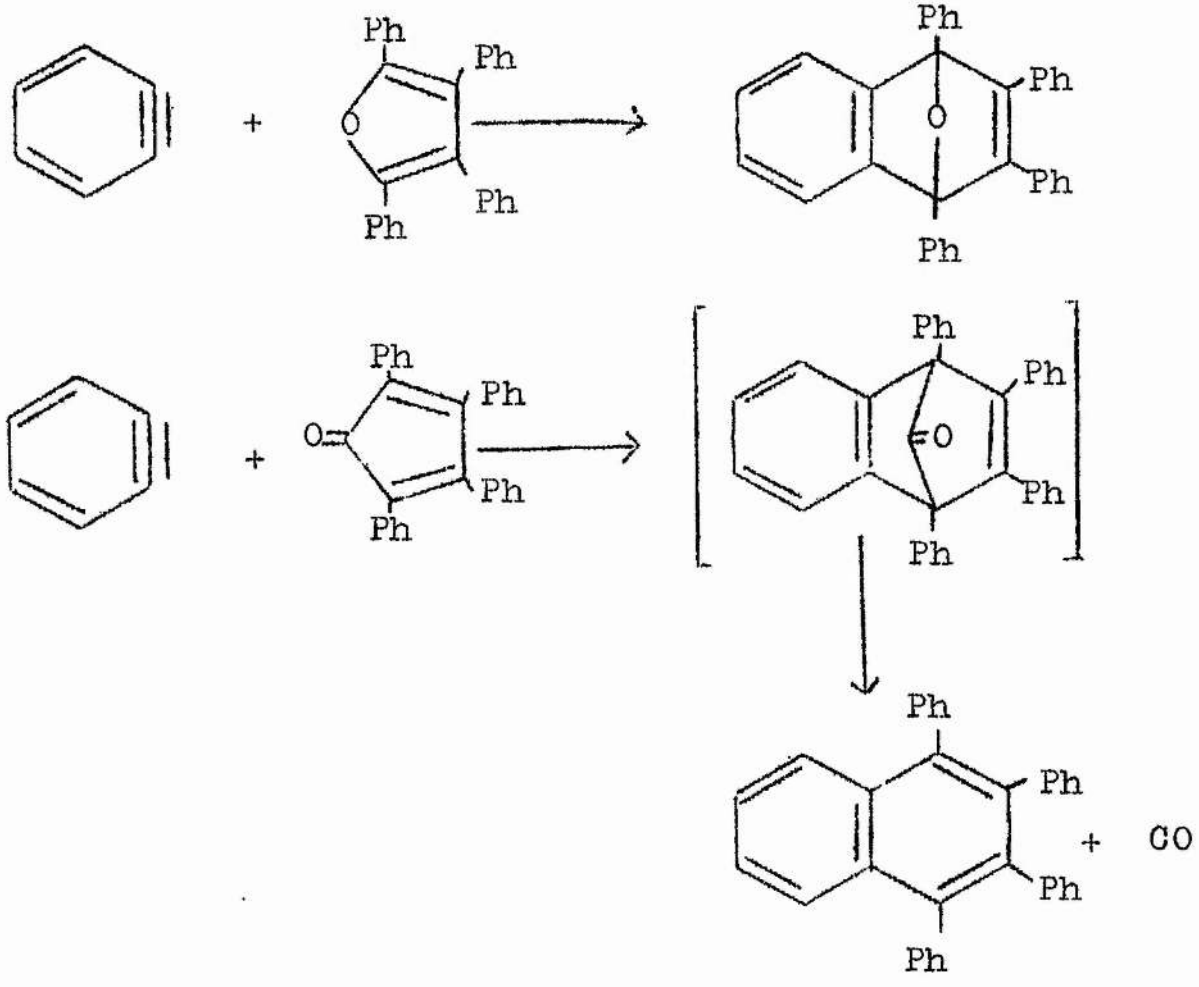
The tendency to participate in cycloaddition reactions is a feature of olefins and alkynes activated by electron-withdrawing substituents, and in olefins where the ring strain is pronounced. It is not surprising therefore that benzyne has been shown to enter into cycloaddition reactions readily.

Wittig and Pohmer [90] showed that benzyne generated from o-fluorobromobenzene and lithium amalgam, gave

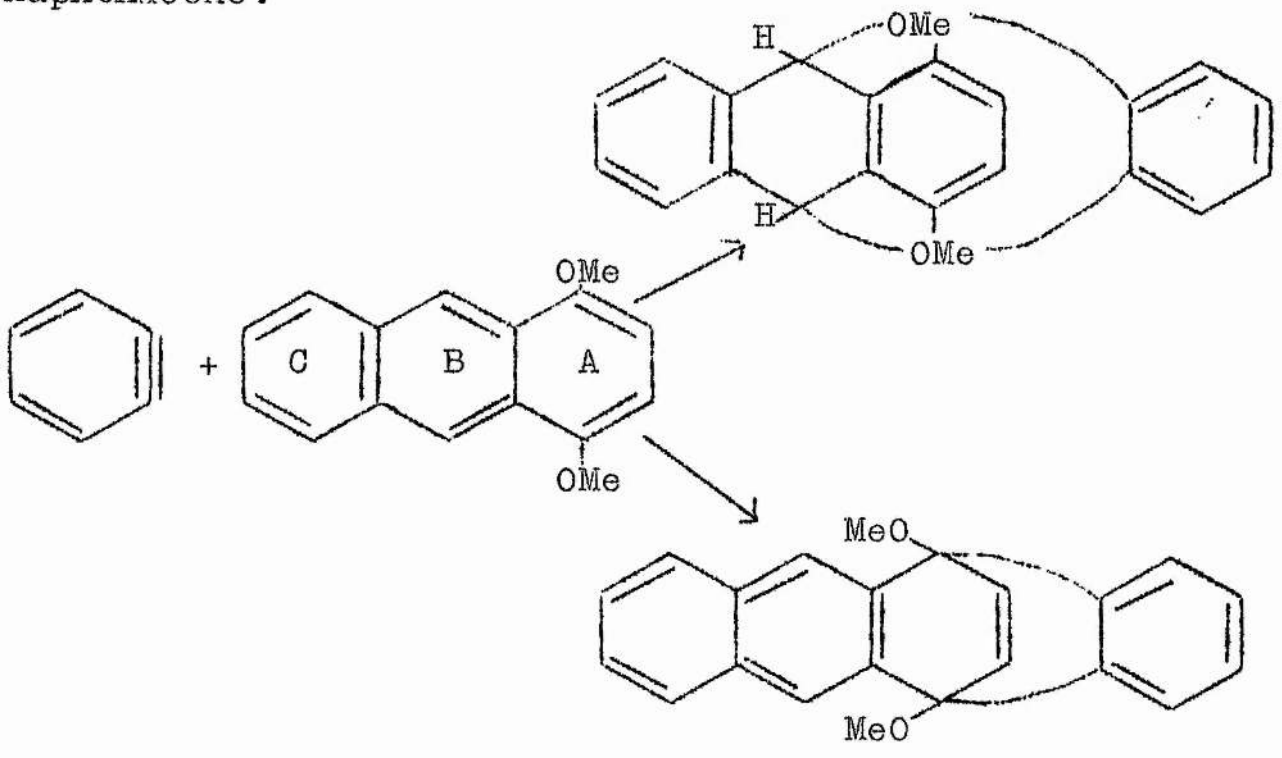
1,4-dihydronaphthalene-1,4-endoxide with furan via a



1,4-addition. Similar reactions occur with 2,3,4,5-tetraphenylfuran [91] and 2,3,4,5-tetraphenylcyclopentadienone [91], though the adduct formed from the latter does not stop at the intermediate, and loses carbon monoxide to form 1,2,3,4-tetraphenylnaphthalene.



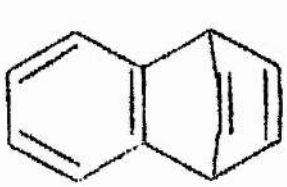
Benzyne intermediacy has been shown to provide a useful synthetic route to triptycene and its substituted derivatives [92,93] by reaction with anthracene, but Klanderman and Criswell [94,95,96] have shown that in addition to the B-ring adduct, a lesser amount of the A-ring adduct was formed, and the relative amount of this A-ring adduct was increased if electrophilic substituents were present at positions 9 and 10, or if nucleophilic substituents were present at positions 1 and 4; thus the reaction of benzyne with 1,4-dimethoxyanthracene gave 1,4-dimethoxytriptycene and 5,12-dimethoxy-5,12-dihydro-5,12-ethenonaphthacene:



Klanderman and Criswell [95] have measured the ratio

of B-ring adduct to A-ring adduct, and shown it to be a constant for a variety of benzyne precursors, thus showing that the properties of benzyne are independent of its source.

Benzene itself has been shown to act as an arynophile, and Miller and Stiles [97,98] have identified benzobicyclo [2,2,2] octatriene (2%),(9), benzocyclo-octatetraene (8%),(10) and biphenyl (6%), (11), from the reaction of benzyne with benzene.



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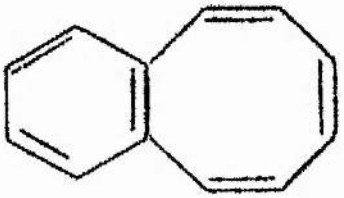
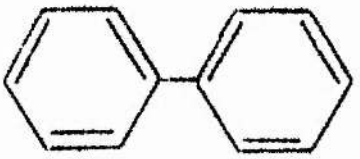


(10)

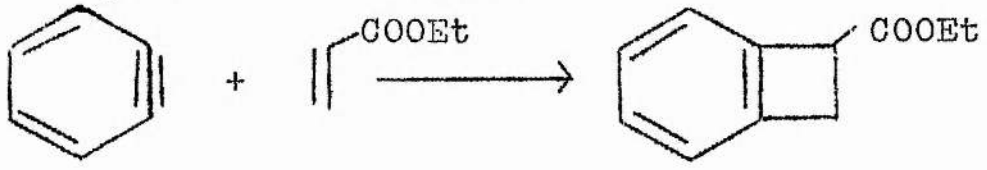


(11)

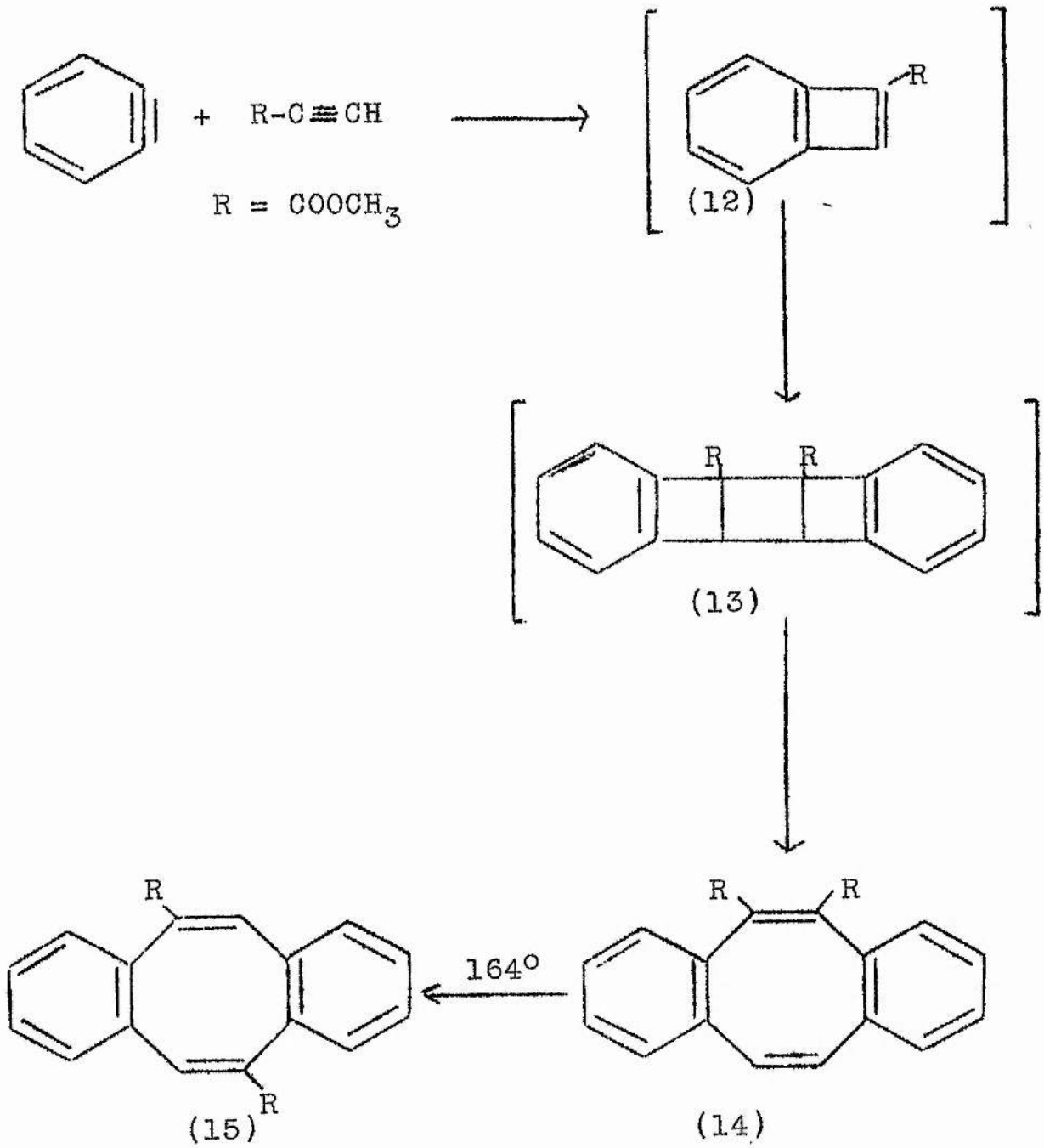
Friedman [99] later showed that the high yield of biphenyl and benzocyclo-octatetraene was due to silver ion contamination in Miller and Stiles' benzyne precursor, and showed that in the absence of silver ions, the major product was benzobicyclo [2,2,2]octatriene (17%), (9).

Benzocyclobutane derivatives have been formed from the reaction of benzyne with acrylonitrile [100] and ethyl acrylate [100] in a 1,2-addition:

e.g.,



Reaction of benzyne with methyl propiolate[101] has been shown to give 5,6-dicarbomethoxydibenzo-[a,e] cyclooctatetraene (14), which when heated at 164° in decalin, isomerises to the 5,11-isomer (13).



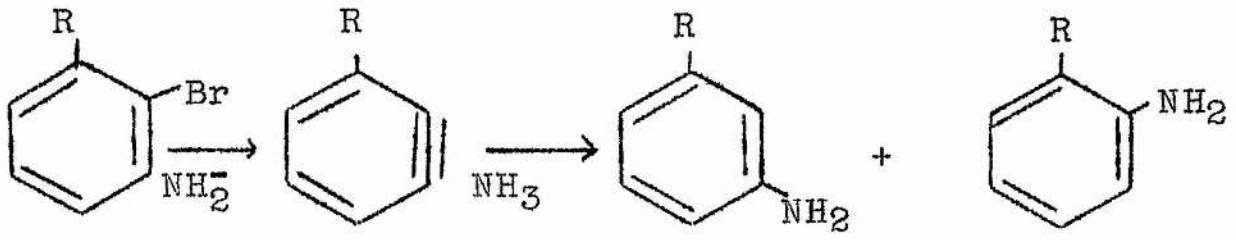
The formation of (14) is best rationalised by assuming

intermediate formation of the benzocyclobutadiene (12) which then dimerises to (13) and isomerises to (14).

The 1,3-addition reactions of benzyne are reviewed extensively elsewhere [102].

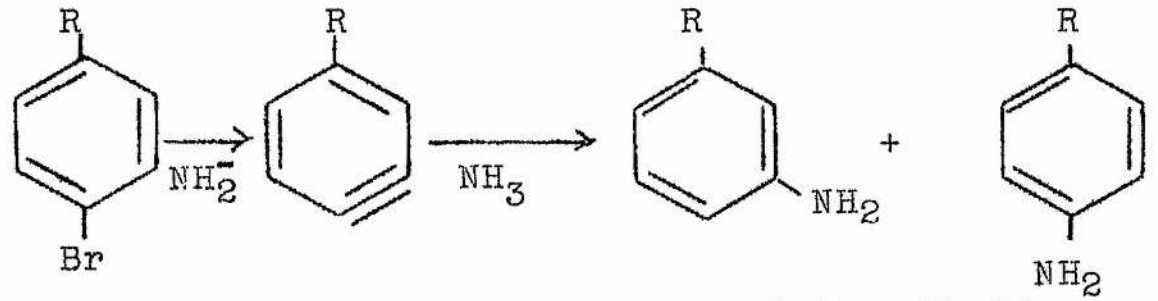
Benzyne has a pronounced electrophilic character as has been shown by the reaction with potassamide in liquid ammonia, and by the addition of phenyl-lithium. The orientation of addition to a substituted benzyne depends not only on the electronic nature of the group present in the aryne but also on its size and on the nucleophilicity of the attacking agent. De Graaff , den Hertog and Melger [103] have investigated the orientation of amide addition to monosubstituted benzynes , and found that the yield of meta isomer formed from 3-substituted benzyne was higher when the substituent in the aryne had a strong negative inductive effect (--I); conjugative (M) effects were found to be less important. In the addition of amide to 4-substituted benzyne, the inductive effect of a substituent in the 4-position , being further from the dehydro bond, exerts less influence, and conjugative effects now assume importance.

Orientation of amide addition to 3-substituted benzyne



		Relative Yields	
R =	CN (--I, -M)	85-90	10-15%
	OCH_3 (--I,++M)	95-100	0-5%
	CH_3 (+I,+M)	45	55%
	O^- (++I,++M)	10-15	85-90%

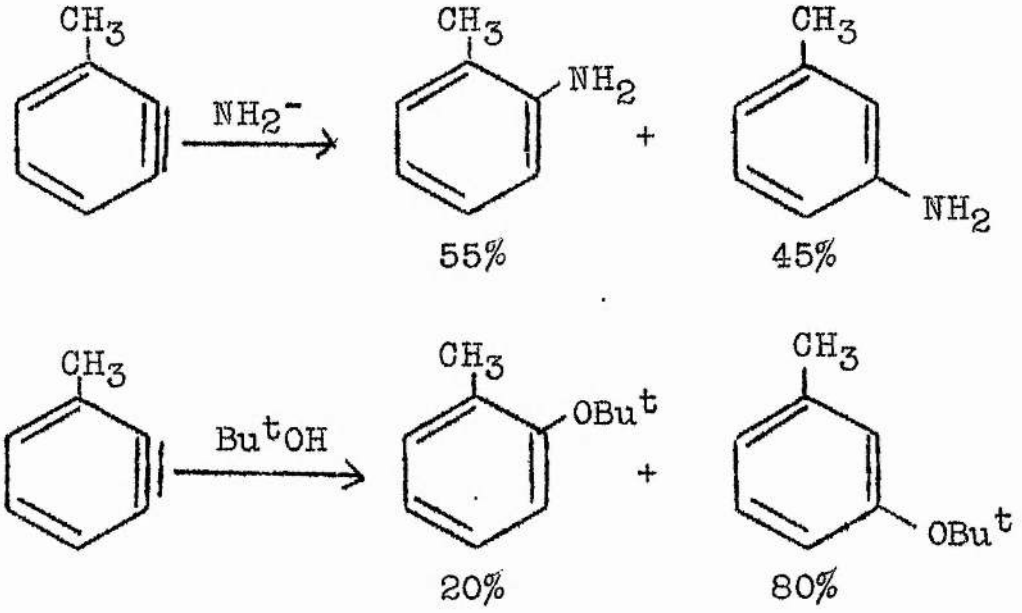
Orientation of amide addition to 4-substituted benzyne



		Relative Yields	
R =	CN (--I, -M)	0-5	95-100%
	OCH_3 (--I,++M)	45-50	50-55%
	CH_3 (+I,+M)	60	40%
	O^- (++I,++M)	100	0%

Cadogan, Hall and Sharp [104] have investigated the steric effects present in the addition of the bulky t-butoxide anion to a monosubstituted benzyne

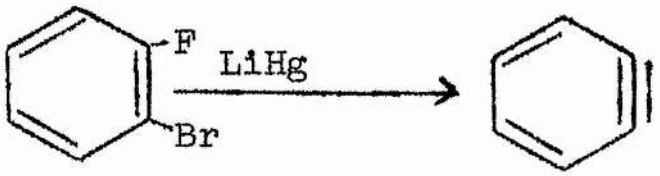
and found a lower percentage of ortho addition to 3-substituted benzyne than would be expected for the addition of amide anion. This they attributed to steric



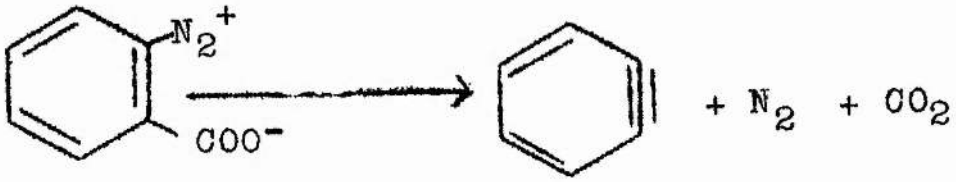
hinderance to addition; the results shown represent relative yields only.

B Sources of arynes

We have seen how Wittig [83] and Roberts [87] and their colleagues used the reaction of fluorobenzene and chlorobenzene with strong base as a source of benzyne, but reactions of this sort are limited in their application. Thus it was not surprising that the reactions of benzyne with nonpolar reagents were first detected [90] only after ways had been found of generating benzyne in the absence of polar compounds:

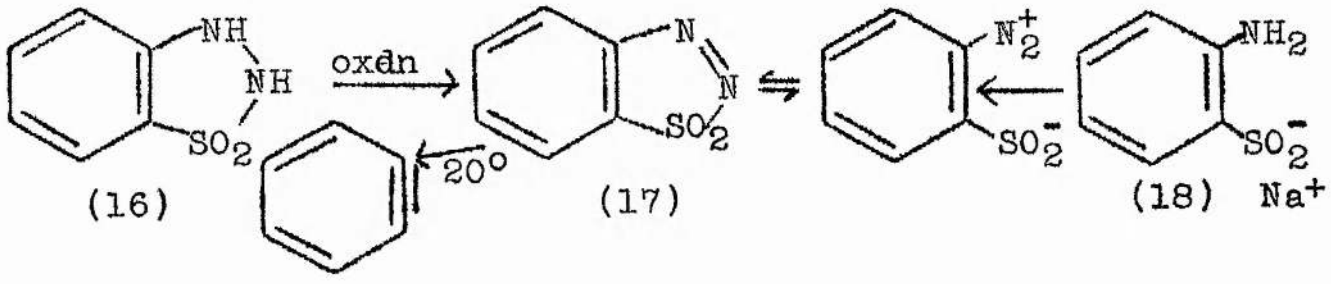


Benzenediazonium-2-carboxylate [97,98,105,106] decomposes smoothly at room temperature in an aprotic solvent to give benzyne, carbon dioxide and nitrogen:

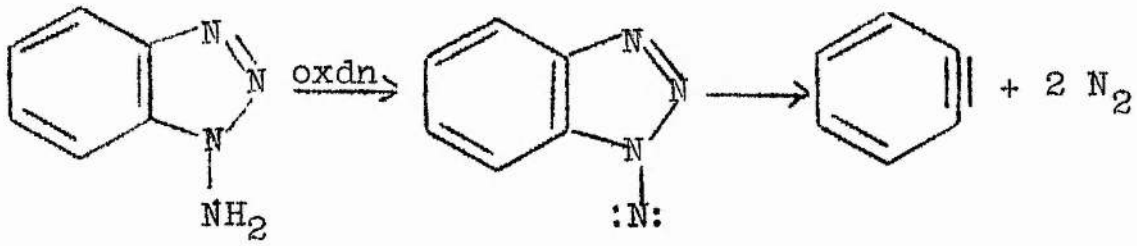


While a more convenient modification of this method is the in situ diazotisation of anthranilic acid with pentyl nitrite [93].

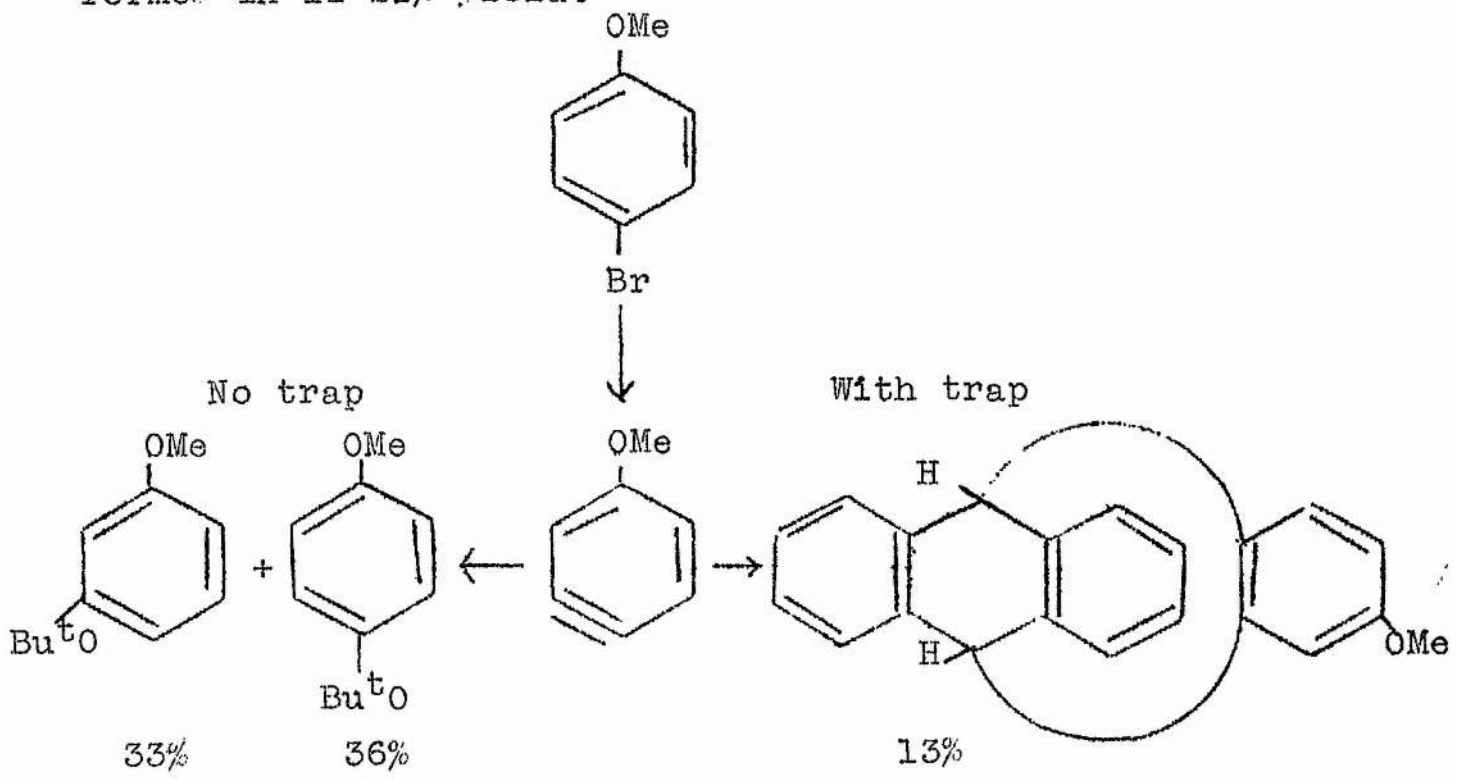
Lead tetraacetate oxidation of amino compounds has been used with success by other workers; thus Wittig and Hoffmann [107] oxidised 1,2,3-benzothiadiazolin-1,1-dioxide (16) to 1,2,3-benzothiadiazole-1,1-dioxide (17) which decomposed readily at 20° to benzyne. The diazotisation of 2-aminobenzenesulphinic acid (18) gave the same result.



Rees and Campbell [108] have oxidised 1-aminobenzotriazole to give benzyne in good yield, possibly via a nitrene intermediate:



Cadogan, Hall and Sharp [104] have used the reaction of potassium t-butoxide with various monosubstituted aryl bromides in t-butylbenzene to prepare arynes. In the absence of an aryne trap, the isomeric aryl t-butyl ethers were formed, and when anthracene was present, triptycenes can be formed in 11-21% yield.



Photolysis of benzenediazonium-2-carboxylate[109,110], 1,2,3-benzothiadiazole-1,1-dioxide [107], o-di-iodobenzene [111,112], 2-iodophenylmercuric iodide [113,114] and bis-2-iodophenyl mercury [113,114] all gave benzyne in varying yields. The high temperature thermolysis of many compound has also been shown [102] to give benzyne in fair yields, but the applications of these techniques lie outside the scope of this work.

IV PROGRAMME OF RESEARCH

At the outset of this investigation, two problems existed. First, the question of the identity and genesis of the arynoid species in the decompositions of acylarylamines, and second, the nature of the decomposition of the latter in halogenomethanes. Experiments designed to throw light on both these problems were therefore carried out.

EXPERIMENTAL

Symbols and Abbreviations

M^+	mass of molecular ion
g.l.c.	gas liquid chromatography
t.l.c.	thin layer chromatography
m/100m	moles per 100 moles of starting material
m.p.	melting point
b.p.	boiling point
i.r.	infra-red
n.m.r.	nuclear magnetic resonance
s	singlet
d	doublet
e.s.r.	electron spin resonance
u.v.	ultraviolet
R_f	ratio of distance moved by the substance to the distance moved by the solvent front

EXPERIMENTAL

Gas Liquid Chromatography. - Four instruments were used for analytical and quantitative investigations: a Varian Aerograph 1520B chromatograph, with flame-ionisation detector, using 2 m x 2.2 mm i.d. packed columns, a Pye 104 chromatograph, with flame-ionisation detector, using 1.5 m x 4 mm i.d. packed columns, a Griffin and George D.6. chromatograph with gas density balance, using 2 m x 5.0 mm i.d. packed columns and a Perkin-Elmer F.11 chromatograph, with flame ionisation detector, using 50 m x 0.25 mm i.d. capillary columns. Quantitative measurements were made with the D.6. instrument using the technique of Cadogan and Sadler[115], or using the 1520B after calibration of the instrument with known mixtures of authentic sample and internal standard, the technique being that described by Hibbert[22]. All authentic samples and internal standards were purified before use. For preparative g.l.c. a Pye 105 model 15 and the Griffin and George D.6. were used. In all cases the carrier-gas was nitrogen, the flow rates and split ratios being as recommended by the manufacturers. The following stationary phases, supported on 100-120 mesh celite were employed: Neopentylglycol succinate (NPGS), polyethyleneglycol adipate (PEGA), fluorosilicone oil

(QF-1), silicone grease (SE-30), apiezon L grease (APL) and xylenol phosphate (XP).

Column Chromatography. - Alumina was Spence and Sons, Grade H, 100-200 mesh (Brockmann activity = 2). Silica gel was Whatman Chromedia SG 31.

Thin Layer Chromatography. - Chromatograms were obtained on 0.3 mm layers of alumina (Merck, Aluminium oxide G), or silica gel (Macherey, Nagel and Co., Silica Gel G). Components in the developed chromatogram were detected by their fluorescence in u.v. light or by their reaction with iodine.

Nuclear Magnetic Resonance Spectroscopy.- A Perkin-Elmer Model R-10 Nuclear Magnetic Resonance Spectrometer operating at a frequency of 60 MHz, and a probe temperature of 35.5°, and a Varian HA-100 Nuclear Magnetic Resonance Spectrometer operating at a frequency of 100 MHz, and a probe temperature of 28° were used. Chemical shifts are recorded as (τ) values, in parts per million, tetramethylsilane being the internal reference. Spectra were determined on 10-15% w/v solutions in carbon tetrachloride, deuterochloroform or occasionally trifluoroacetic acid.

Mass Spectroscopy. -Mass Spectra were obtained using an Associated Electrical Industries MS-902 mass spectrometer.

Spinning-Band Column Distillation. These were performed with a Nester-Faust Annular Teflon Spinning-Band Distillation Column. A reflux ratio of 30:1 and a distillation rate of approximately 1 ml per hour were employed.

Melting Points. - Melting points of all new compound were determined using a Kofler hot stage apparatus.

Elemental Analyses. - Microanalyses were performed by Mr.J.Bews, University of St.Andrews and Mr.B.Clark, University of Edinburgh.

Solvents and Reagents. - Benzene, ether and petroleum ether, (fraction with boiling point 40-60°) unless otherwise stated), were purified by distillation and dried over sodium. Carbon tetrachloride, methylene chloride, chloroform, bromoform, methylene bromide and bromotrichloromethane were purified by distillation using a 1 m helix-packed column. A large centre portion of distillate was collected and its purity checked by g.l.c. In the case of bromotrichloromethane, methylene bromide and bromoform, the distillation apparatus was protected from light with aluminium foil. Furan was passed down an alumina column, distilled and dried over sodium. Super-dry ethanol was prepared as described by Vogel[116]. Pyridine was dried over sodium hydroxide

pellets and distilled. Deuteroacetic acid (Koch Light 98%) was used without purification. Potassium t-butoxide was sublimed, block temp.200°/0.02 mm. All other reagents were purified by distillation or recrystallisation.

Infra-red Spectroscopy. - Perkin-Elmer models 257 and 337 were most commonly used for infra-red spectroscopy. A Unicam S.P.200 was used occasionally. Liquid samples were examined as thin films; solid as melts or Nujol mulls. Solution spectra were obtained with matched sodium chloride solution cells of path length 0.1 mm.

Ultraviolet Spectroscopy. - A matched pair of 1 cm silica cells were used with a Unicam S.P. 800 Ultraviolet Spectrometer.

I PREPARATION OF ACYLARYLAMINES

A o-, and p-t-Butylacetanilides

o-,m-, and p-t-Butylnitrobenzenes. - t-Butylbenzene(178g, 1.32 moles) was nitrated by the method of Nelson and Brown[117]. The crude product was distilled to give a colourless liquid b.p.76-86°/23 mm and an oil (180g),b.p.63-87°/0.15 mm, which was shown by g.l.c. (2% NPGS/150°) to be a mixture of o-, m-, and p-t-butylnitrobenzenes in the approximate ratio 2:1:5. Fractional distillation using the spinning-band

column yielded o-t-butylnitrobenzene, b.p.128°/17.5 mm and m-t-butylnitrobenzene, b.p.143°/17.5 mm. p-t-Butylnitrobenzene, m.p.27°, was obtained by crystallisation of the residue from ethanol at -40°.

p-t-Butylaniline. - A mixture of p-t-butylnitrobenzene (35.8g, 0.20 moles), iron powder (44.8g), ethanol (80g), and water (80g) was stirred while hydrochloric acid (sp.gr.1.16, 4.8g) was added. After stirring under reflux for 14 hr, the cooled reaction mixture was made alkaline with 10% sodium hydroxide solution and filtered through celite, which was then washed with **methanol.** The alcohol was distilled and the residue extracted with ether (400 ml). The ether extract was dried over anhydrous magnesium sulphate and potassium hydroxide pellets and evaporated to give a brown oil which was distilled under dry nitrogen to give p-t-butylaniline (27.9g, 94%), b.p.108-110°/10 mm.

p-t-Butylacetanilide.- Acetic anhydride (22.5g) was gradually added to a stirred solution of p-t-butylaniline (26.7g, 0.179 moles) in acetic acid (12.0g). The mixture was heated at 120° for 30 min. The solid which separated when the hot solution was poured into ice-water (1000 ml) was collected, washed with water, dried and recrystallised from benzene/petroleum (6:1) to give p-t-butylacetanilide (32.8g, 96%), m.p.173-4°,

(lit.,[118] 174°).

B N-Acylanthranilic Acids. N-Acetylanthranilic acid, (yield 85%), m.p. 183°, (lit.,[119] 181-2°) and N-formylanthranilic acid, (yield 90%), m.p. 167° (lit.,[119] 167°) were prepared by acylation of anthranilic acid as described by Zentmyer and Wagner [119].

C Other Acylarylamines. - The following acylarylamines were prepared in 57-81% yield from the corresponding amine and acid anhydride in the manner described for p-t-butylacetanilide:

propionanilide, m.p.105° (lit.,[120] 105-6°),

isobutyranilide, m.p.104° (lit.,[120] 104-5°),

p-methoxyacetanilide, m.p.137-8° (lit.,[120] 130-2°),

p-carbethoxyacetanilide, m.p.110° (lit.,[120] 110°),

m-bromoacetanilide, m.p.87° (lit.,[120] 87.5°),

o-t-butylacetanilide, m.p.163.5-4° (lit.,[118] 163°).

Formanilide was prepared from aniline and formic acid (98-100%) in 70% yield, m.p.49-50° (lit.,[120] 50°). Acetanilide, m.p.114-5° and p-nitroacetanilide, m.p.215-7° were purified by recrystallisation of commercially available samples.

II PREPARATION OF ARYL ESTERS

A o-, m-, and p-t-Butylphenyl acetates. - o-t-Butylphenyl acetate, b.p.116°/12 mm, mt-butylphenyl acetate, m.p.42-3°

and p-t-butylphenyl acetate, b.p.130/16 mm were prepared by Dr.M.J.P.Harger[128].

B Phenyl Formate

Silicoformic Anhydride. - Formic acid (92.0g, 98-100%) and silicon tetrachloride (85.0g) were allowed to react in benzene (150 ml) at 60° till evolution of hydrogen chloride ceased. After 1 hr at 100°, the solvent and excess formic acid were removed by distillation to give crude (contains SiO_2) silicoformic anhydride (80g).

Phenyl Formate. - Silicoformic anhydride (52g), phenol (47g) and benzene (100 ml) were heated at 100° for 5 hr, then distilled to give crude phenyl formate (38g), b.p.172-80°. This was purified by heating with silicon tetrachloride to remove phenol and subsequent distillation gave pure phenyl formate, (19g, 31%), b.p.178° (lit.,[121] 178°).

N.m.r. (CCl_4): τ 2.5-3.1 (complex, 5H) and 1.83 (s, 1H).

C Phenyl Propionate. - Thionyl chloride (12 ml) was added to phenol (15g) and propionic acid (13.3g) and heated till evolution of hydrogen chloride and sulphur dioxide ceased. Distillation afforded phenyl propionate, (19.0g, 70%), b.p.211° (lit.,[120] 211°).

Phenyl isobutyrate was prepared similarly in 81% yield, b.p.99°/12 mm (lit.,[127] 118-9°/35 mm).

D Other Esters

The following acetates were prepared from the corresponding phenol using the method described by Vogel[116] for the preparation of p-nitrophenyl acetate:

p-chlorophenyl acetate, b.p.88°/0.15 mm,

p-methoxyphenyl acetate, m.p.31-3°,

m-bromophenyl acetate, b.p.58°/0.03 mm, p- m.p.21°,

p-nitrophenyl acetate, m.p.78°,

p-carbethoxyphenyl acetate, m.p.35°.

III PREPARATION OF ARYL HALIDES

A m-, and p-t-Butylchlorobenzenes. - Chlorobenzene (169g) was t-butylated by the method of Lerer and Fabre[122]. The crude product was distilled to give a colourless liquid (113 g), b.p.25-40°/9 mm and an oil (33.0g), b.p.81°/9 mm. The latter was examined by g.l.c. (6% XP/119°) and found to be a mixture of m-, and p-t-butylchlorobenzenes in the approximate ratio 4:1. Pure samples of m-, and p-t-butylchlorobenzene were obtained by preparative g.l.c. (17 ft x 0.375 in 6% XP column at 119°).

N.m.r. ($CDCl_3$): m-t-Butylchlorobenzene: τ 2.64-3.05 (complex, 4H) and 8.64 (s, t-butyl).

p-t-Butylchlorobenzene: τ 2.57 (s, 4H) and 8.68 (s, t-butyl).

B o-t-Butylchlorobenzene

2-Chloro-4-nitro-t-butylbenzene. - p-Nitro-t-butylbenzene was chlorinated by the method of Lerer and Fabre[122] to give 2-chloro-4-nitro-t-butylbenzene (28g, 72%), m.p.92° (lit.,[122] 92°).

3-Chloro-4-t-butylaniline hydrochloride. - 2-Chloro-4-nitro-t-butylbenzene (28g) was reduced as described for p-t-butylnitrobenzene. Addition of hydrochloric acid to the filtered reaction mixture precipitated 3-chloro-t-butylaniline hydrochloride (29g, 97%).

o-t-Butylchlorobenzene. - 3-Chloro-4-t-butylaniline hydrochloride (28g) and water were stirred in a 2 l beaker while hydrochloric acid (60 ml) was added. The mixture was cooled to -5° and a solution of sodium nitrite (9.25g) in water (33 ml) was added over 1 hr keeping the temperature between -5° and 0°. Hypophosphorous acid (330 ml, 30%) at -5° was added and the reaction mixture left for 24 hr at 0°. The lower layer was separated and the aqueous layer extracted with ether (3 x 100 ml). The combined organic layers were washed with potassium hydroxide solution (20 ml, 50%), water (100 ml) and dried over anhydrous magnesium sulphate. The ether was evaporated and the residual liquid fractionally distilled to give pure o-t-butylchlorobenzene (5g, 23%) b.p.95-6°/16 mm (lit.,[122] 98°/25 mm).

N.m.r. (CCl_4): τ 2.6-3.2 (complex, 4H) and 8.6 (s, t-butyl).

o-t-Butylbromobenzene prepared similarly had b.p.130-2°/40 mm (lit.,[124] 96-8°/12 mm).

N.m.r. (CCl_4): τ 2.38-3.26 (complex, 4H) and 8.50 (s,t-butyl).

C m-t-Butylbromobenzene

2-Bromo-4-t-butylacetanilide. - Bromine (25.3g) was added to a suspension of p-t-butylacetanilide (30g) in water (200 ml). The solid which separated was filtered and recrystallised from ethanol to give 2-bromo-4-t-butylacetanilide (37.5g, 89%), m.p.155-6°, (lit.,[125] 153°).

2-Bromo-4-t-butylaniline. - 2-Bromo-4-t-butyl acetanilide (15g) was heated under reflux in a mixture of sulphuric acid (23.7g) and water (60.3 ml) for 15 hr. The mixture was allowed to cool and neutralised with sodium hydroxide solution (20%). The amine was extracted with ether (4 x 100 ml), washed with water and dried over anhydrous magnesium sulphate. The ether was evaporated and the residue (12.0g) used directly in the next stage.

m-t-Butylbromobenzene. - 2-Bromo-4-t-butyl-aniline (11.0g) was deaminated as described for o-t-butylchlorobenzene to give m-t-butylbromobenzene, (7.4g, 72%), b.p.106-7°/16 mm, (lit.,[123] 103-6°/17 mm).

N.m.r. (Neat): τ 2.35-3.15 (complex, 4H) and 8.83 (s, t-butyl).

D m-Nitrofluorobenzene

m-Nitrobenzenediazonium fluoroborate. - m-Nitroaniline (45g) was dissolved in a mixture of water (126ml) and hydrochloric acid (126ml) at 0°. To this was added a solution of sodium nitrite (36.5g) in water (75 ml) over 1 hr while maintaining the temperature at 0°. A chilled solution of sodium fluoroborate (76g) in water (150 ml) was added slowly and the mixture allowed to stand for 10 min with frequent stirring. The precipitate was filtered, washed with ice-water (30 ml), methanol (15 ml) and ether (30 ml) and dried over phosphorus pentoxide at 0.05 mm, m.p. (decomp) 145°.

m-Nitrofluorobenzene. - The fluoroborate from above was decomposed as described by Vogel [116] for the preparation of fluorobenzene, to give, after distillation, m-nitrofluorobenzene (9.7g, 21%), b.p. 86°/19 mm, (lit.,[126] 200°).

N.m.r. (Neat): τ 1.85-2.70 (complex).

I.r. (Neat): 1520 and 1350 cm^{-1} (nitro).

All other aryl halides were purified from commercially available samples by distillation or crystallisation.

IV PREPARATION OF ARYNOPHILES

A 2,5-di-p-Methylsulphonylphenyl-3,4-diphenylcyclopentadienone

p-Acetylthioanisole. - Thioanisole (200g) was acetylated by the method of Gregory[129] to give p-acetylthioanisole (180g, 70%), b.p.90-111°/0.1 mm, (lit.,[129] 134-40°/0.35 mm).

p-Thioanisylacetic acid. - p-Acetylthioanisole (100g) was converted to p-thioanisylacetic acid (70g, 70%), m.p.92-4°(lit.,[130] 92-4°) by the method of Corse et al.[130].

Ethyl p-thioanisyl acetate. - p-Thioanisylacetic acid (70g) was esterified by heating under reflux in ethanol (250 ml) with sulphuric acid (5g). The ethanol was distilled off and the residue taken up in ether, washed with sodium bicarbonate solution and water, dried and the solid residue which remained after the ether was evaporated was recrystallised from petrol to give ethyl p-thioanisyl acetate (70g, 86%), m.p.55-6°, (lit.,[139] 55.5-56.2°).

1,3-di-p-Thioanisylpropan-2-one. - Ethyl p-thioanisyl acetate (50g) was self condensed using isopropyl magnesium bromide as described by Coan et al.[132] for the preparation of 1,3-di-p-methoxyphenylpropan-2-one

to give the acetoacetic ester (crude 55g). This was hydrolysed and decarboxylated by heating under reflux with acetic acid (500ml) and hyirochloric acid (70 ml, 18%) for 5 hr. The mixture was evaporated to low volume and extracted with ether, washed with sodium hydroxide (10%), water and then dried. Evaporation of the ether left a solid which was recrystallised from hexane to give 1,3-di-p-thioanisylpropan-2-one (25g, 64%), m.p.79-80°.

(Found: C, 67.31; H, 6.01. $C_{17}H_{18}OS_2$ requires C, 67.55; H, 5.96%).

N.m.r. ($CDCl_3$): τ 2.72-3.80 (A_2B_2, 8H), 6.37 (CH_2, 4H), and 7.77 (CH_3, 6H).

I.r. (Nujol): 1690 cm^{-1} (C=O).

1,3-di-p-Methylsulphonylphenylpropan-2-one. - To a solution of 1,3-di-p-thioanisylpropan-2-one (10g) in acetic acid was added dropwise hydrogen peroxide solution (23.2g, 100 vol). The solution was heated under reflux for 20 hr and after cooling, addition of water (5 ml) induced crystallisation of pure 1,3-di-p-methylsulphonylphenylpropan-2-one (8.5g, 71%), m.p.187-8°.

(Found: C, 55.58; H, 4.87. $C_{17}H_{18}O_5S_2$ requires C, 55.7; H, 4.92%).

I.r. (Nujol): 1680 (C=O) and 1080 cm^{-1}(S=O).

2,5-di-p-Methylsulphonylphenyl-3,4-diphenylcyclopentadienone. - To a solution of 1,3-di-p-methylsulphonylphenylpropan-2-one (7.32g, 0.02 moles) and benzil (4.2g, 0.02 moles) in ethanol (50 ml) heated under reflux at a temperature slightly lower than the boiling point, was added benzyltrimethylammonium hydroxide (3.0g, 40% in water) and the solution heated under reflux for 10 min. The cooled solution was filtered and the precipitate recrystallised from acetic acid to give 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone (1.5g, 14%), m.p.299-300°. (Found: C,68.66; H,4.37. $C_{31}H_{24}O_5S_2$ requires C,68.9, H,4.44%).

N.m.r. ($CDCl_3$): 2.05-3.16 (complex, 14H) and 6.97 (s, CH_3-, 6H).

I.r. (Nujol): 1710 (C=O) and 1080 cm^{-1}(S=O).

B 2,3,4,5-Tetraphenylcyclopentadienone

Benzil (50g) and dibenzyl ketone (50g) were condensed as described for 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone using potassium hydroxide (0.5g) in ethanol (5 ml) as the condensing agent to give, after recrystallisation from benzene/ethanol (1:1), 2,3,4,5-tetraphenylcyclopentadienone (81.6g, 90%), m.p.222°, (lit.,[131] 218°).

C 2,5-di-p-Methoxyphenyl-3,4-diphenylcyclopentadienone

This compound was prepared from benzil (10.1g) and 1,3-di-p-methoxyphenylpropan-2-one (13.0g) as described by Coan et al.[132] to give, after recrystallisation from benzene/ethanol (1:1), 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (15g, 70%), m.p.195-6°, (lit.,[132] 195.2-6°).

D 2,5-di-p-Methylphenyl-3,4-diphenylcyclopentadienone

This compound was prepared as described by Coan et al.[132] in 73% yield, m.p.179-80°, (lit.,[132] 179-180.2°).

E 1,4-Dimethoxyanthracene

1,4-Dimethoxyanthraquinone. - 1,4-Dihydroxyanthraquinone (30g) was methylated with methyl p-toluenesulphonate in 1,2,3-trichlorobenzene (50g) as described by Zahn and Ochwat[133] to give 1,4-dimethoxyanthraquinone (20g, 60%), m.p.168-9°, (lit.,[133] 170-1°).

1,4-Dimethoxy-9,10-dihydro-9,10-dihydroxyanthracene. - 1,4-Dimethoxyanthraquinone (20g) was reduced with sodium borohydride (20g) in methanol (1000 ml) as described by Lepage[140] to give, after recrystallisation from xylene, 1,4-dimethoxy-9,10-dihydro-9,10-hydroxyanthracene (14g, 68%), m.p. 152°, (lit.,[140] 152-3°).

1,4-Dimethoxyanthracene. - 1,4-Dimethoxy-9,10-dihydro-9,10-dihydroxyanthraquinone (10g) was warmed with titanous chloride (35g) in methanol (250 ml) and poured into water (2000 ml). Chromatography of the precipitate on alumina eluting with benzene/petrol (1:4) gave, after recrystallisation from acetic acid, 1,4-dimethoxyanthracene (7.0g, 80%), m.p.136-7°, (lit.,[134] 137°).

F 9,10-Dimethoxyanthracene. This compound was made from anthraquinone by Meyer's method[135] in 60% yield, and recrystallised from acetic acid, m.p.200-1°, (lit.,[135] 202°).

G 9,10-Dimethylanthracene. - Anthraquinone (50g), magnesium (25g), iodomethane (75 ml), benzene (600 ml), and ether (300 ml) were heated together on a water bath under reflux for 2 hr. After cooling, the solution was gradually added to hydrogen iodide (120 ml, 50% in water) and methanol (400 ml) at 0°. Acetic acid (400 ml) was added and the yellow precipitate of 9-methyl-10-iodomethylanthracene filtered and dried.

A solution of 9-methyl-10-iodomethylanthracene (13.5g) in dioxan (840 ml) and hydrochloric acid (42 ml) was added to stannous chloride (140g) in a mixture of dioxan (700 ml) and hydrochloric acid (420 ml). The solution was heated under reflux for 5 min and allowed

to stand for 1 hr. Water (8 l) was added, and the product filtered and chromatographed on alumina. Elution with benzene/petrol (1:4) gave after recrystallisation from ethanol, 9,10 dimethylanthracene (6.5g,15%), m.p.179-80°, (lit.,[136] 179-80°).

H 9-Nitroanthracene. - This compound was prepared as described in "Organic Synthesis",[137] in 68% yield, m.p.146°, (lit.,[137] 145-6°).

I 9-Bromoanthracene. - This compound was prepared as described by Barnett and Cook[138] in 80% yield, m.p. 98°, (lit.,[138] 98-9°).

J Other Arynophiles

Anthracene (B.D.H."blue fluorescence") was dried over phosphorus pentoxide in a vacuum dessicator. Furan was distilled, dried over molecular seive, and redistilled from sodium wire, b.p.31°, immediately before use.

V PREPARATION OF ARYNE SOURCES

A o-t-Butylbromobenzene. -This compound has already been described.

B 1-Aminobenzotriazole. - This compound was prepared in 14% yield from benzotriazole using hydroxylamine-O-sulphonic acid as described by Rees and Campbell[108] m.p.83°, (lit.,[108] 83-4°).

C Other Aryne Sources

Anthranilic acid was recrystallised from benzene containing a little ethanol, and had m.p. 145-6°, (lit.,[120] 144-6°).

VI PREPARATION OF ARYNE ADDUCTS

A 1,4-Dihydronaphthalene-1,4-endoxide

1,4-Dihydronaphthalene-1,4-endoxide, prepared by Dr.J.T.Sharp, was recrystallised from petroleum and had m.p. 55-6°, (lit.,[141] 55-6°).

B 5-t-Butyl-1,4-dihydronaphthalene-1,4-endoxide

5-t-Butyl-1,4-dihydronaphthalene-1,4-endoxide, prepared by Dr.M.J.P.Harger[128], was recrystallised from petroleum at -60°, and had m.p. 56-7°.

C 1,4-di-p-Methoxyphenyl-2,3-diphenylnaphthalene

A solution of anthranilic acid (0.56g) in acetone (8 ml) was added to a solution of pentyl nitrite(0.57g) and 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (2.0g) in carbon tetrachloride (50 ml) at reflux temperature and the mixture heated under reflux for 1hr. The volatile products were evaporated and the residue chromatographed on alumina (100g). Elution with benzene/petrol (1:4) gave, after recrystallisation from ethanol/carbon tetrachloride (1:1), 1,4-di-p-methoxyphenyl-2,3-diphenylnaphthalene, (2.1g, 95%), m.p.222-3°,(lit.,[142] 221.5-222°).

(Found: C, 88.09; H, 5.97. $C_{36}H_{28}O_2$ requires C, 87.8; H, 5.69%).

N.m.r. ($CDCl_3$): τ 2.24-3.40 (complex, 22H) and 6.26 (s, CH_3, 6H).

D 1,4-di-p-Methylphenyl-2,3-diphenylnaphthalene

Anthranilic acid was diazotised in the presence of 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone (1.87g) as described above to give, after chromatography on alumina, 1,4-di-p-methylphenyl-2,3-diphenylnaphthalene (1.8g, 86%), m.p. 226-226.5° after recrystallisation from ethanol/carbon tetrachloride (1:1). (Found: C, 94.16; H, 6.39. $C_{36}H_{28}$ requires C, 93.91; H, 6.09%).

N.m.r. ($CDCl_3$): τ 2.30-3.20 (complex, 22H) and 7.72 (s, CH_3, 6H).

E 1,4-di-p-Methylsulphonylphenyl-2,3-diphenylnaphthalene

Anthranilic acid (0.188g) was diazotised in the presence of 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone (0.5g) as described above to give, after chromatography, 1,4-di-p-methylsulphonylphenyl-2,3-diphenylnaphthalene (0.5g, 92%), m.p. 339-40°, after recrystallisation from acetic acid. (Found: C, 73.34; H, 4.81. $C_{36}H_{28}O_4S_2$ requires C, 73.35; H, 4.76%).

N.m.r. ($CDCl_3$): τ 2.10-3.32 (complex,22H) and 7.00 (s, CH_3, 6H).

I.r. (Nujol): 1080 cm^{-1} (S=O).

F 1,4-Dimethoxytriptycene and 5,12-Dimethoxy-5,12-dihydro-5,12-ethenonaphthacene

1,4-Dimethoxytriptycene, m.p.239-241°, and 5,12-dimethoxy-5,12-dihydro-5,12-ethenonaphthacene, m.p.156-8° were given by Dr.B.H.Klanderman[96].

G 9,10-Dimethoxytriptycene

To a solution of 9,10-dimethoxyanthracene (0.60g) and pentyl nitrite (0.31g),being heated under reflux in carbon tetrachloride (25 ml), was added dropwise a solution of anthranilic acid (0.30g) in acetone (8 ml). The mixture was heated for a further 1 hr under reflux and the volatile products evaporated. The residue was heated under reflux with maleic anhydride (0.60g) in chlorobenzene (25 ml) for 12 hr and after removal of the solvent, chromatography on alumina (100g), eluting with benzene/petrol (1:9) afforded, after recrystallisation from petrol (b.p. 60-80°),9,10-dimethoxytriptycene (0.40g, 58%), m.p. 191-2°, (lit.,[96] 192-4°).

(Found: C, 84.38; H,5.54. $C_{22}H_{18}O_2$ requires C, 84.1, H, 5.73%). M^+ 314.

H 9-Nitrotriptycene

Anthranilic acid (1.37g) was diazotised with pentyl nitrite (2.23g) as described above. After removal of the unreacted 9-nitroanthracene with maleic anhydride (2.23g) in chlorobenzene (25 ml), chromatography on alumina afforded 9-nitrotriptycene (0.31g, 10%), m.p. 248-50°, (lit.,[143] 241-3).

I 9-Bromotriptycene

Anthranilic acid (1.37g) was diazotised with pentyl nitrite (1.8g) in the presence of 9-bromoanthracene (5.14g) as described above. After removal of the unreacted 9-bromoanthracene with maleic anhydride (5.14g), chromatography afforded 9-bromotriptycene, (0.93g, 28%), m.p. 254.5-255.5°, (lit.,[143] 246-8°).

J Other Aryne Adducts

1,2,3,4-Tetraphenylnaphthalene, m.p. 199-200°, (lit.,[120] 204-204.5°) was recrystallised from acetic acid. Triptycene, m.p. 253-4°, (lit.,[94] 253-4°), was recrystallised from petrol (b.p. 60-80°) containing a little benzene.

VII MISCELLANEOUS REACTIONS

A "Galvinoxyl"

"Galvinoxyl, m.p.160°, (lit.,[144] 153.2-3.6°) was given by the British Petroleum Company Ltd.

B 2,2,6,6-Tetramethyl-4-hydroxypiperidine-N-oxide

2,2,6,6-Tetramethyl-4-hydroxypiperidine-N-oxide, m.p. 70-1°, (lit.,[145] 71.5°), was given by the British petroleum Company Ltd.

C 1,1-Dichloro-2-methyl-2-phenylcyclopropane

1,1-Dichloro-2-methyl-2-phenylcyclopropane was prepared in 48% yield from α-methylstyrene as described by Dale et al.[146] and had b.p.44-6°/0.05 mm, (lit.,[146] 77-81°/5 mm).

D Bicyclohex-2-enyl

Cyclohexene was dimerised in low yield using di-t-butylperoxide, as described by Farmer and Moore[147], b.p.60-7°/0.5 mm, (lit.,[147] 62-3°/0.5 mm).

E Dichloronorcarane

Dichloronorcarane was prepared in 35% yield from cyclohexene as described by Doering et al.[148], and had b.p.79-9°/15 mm, (lit.,[148] 78-9°/15 mm).

F Pentyl Nitrite

Pentyl nitrite was prepared as described by Vogel[116], b.p.103-5°, stored at -10° over molecular seive and redistilled immediately before use.

G Nitrosyl Chloride

Nitrosyl chloride was prepared by the method of

Morton and Wilcox [149], by allowing an aqueous solution of sodium nitrite to react with hydrochloric acid. The product was dissolved in acetic anhydride to give a 30% w/v solution which was stored at -10°.

H 2-Methyl-3,1-benzoxazin-4-one

2-Methyl-3,1-benzoxazin-4-one was prepared from N-acetylanthranilic acid in 83% yield as described by Zentmyer and Wagner [119], m.p. 80-1°,(lit.,[119] 80-1°).

I 3,1-Benzoxazin-4-one

3,1-Benzoxazin-4-one was prepared from N-formylanthranilic acid in 76% yield as described by Zentmyer and Wagner [119], m.p. 43-4°,(lit.,[119] 43-44.4°).

VIII PREPARATION OF ACYLARYLNITROSAMINES

A Acetylarylnitrosamines

1.N-Nitrosoacetanilide. - Acetanilide (10g) and potassium acetate (10g), in a mixture of acetic anhydride (30 ml) and glacial acetic acid (70 ml), were stirred and cooled to 0°. Nitrosyl Chloride (6g) in acetic anhydride (30% w/v solution) was added over 30 min and the mixture stirred for a further 30 min then poured into ice-water (1.5 l) and the precipitate filtered, dried between filter paper, and dried over phosphorus pentoxide at 0.05 mm to give N-nitrosoacetanilide (10g, 83%), m.p.50-1°, (lit.,[150] 50°).

The following acetylarylnitrosamines were prepared similarly, (all decomposed on melting):

p-Methoxy-N-nitrosoacetanilide. - (90% Yield), m.p.71-2°, (lit.,[151] 83-4°).

p-Carbethoxy-N-nitrosoacetanilide. - (55% Yield), m.p.48-9°.

m-Bromo-N-nitrosoacetanilide. - (71% Yield), m.p.47-8°, (lit.,[81] 48-9°).

p-Nitro-N-nitrosoacetanilide. - (87% Yield), m.p.68°, (lit.,[152] 68-70°).

2.o-t-Butyl-N-nitrosoacetanilide. - o-t-Butylacetanilide (11.8g) in a mixture of glacial acetic acid (37g), acetic anhydride (38g) and pyridine (2 ml)

was stirred at 0°. Nitrosyl chloride (6.8g) was added over 30 min and stirring continued for a further 1 hr, then the solution poured into ice-water (1.5 l) and the precipitate filtered and dried as above to give o-t-butyl-N-nitrosoacetanilide (12.1g, 90%), m.p.60° (decomp.),(lit.,[118] 62°,decomp.)

p-t-Butyl-N-nitrosoacetanilide was prepared similarly in 86% yield, m.p.40°(decomp.),(lit.,[118] 57.5°, decomp.).

B N-Nitroso-N-acylanthranilic acids

N-Nitroso-N-formylanthranilic acid. - N-Formylanthranilic acid was nitrosated using the method described for N-nitrosoacetanilide to give N-nitroso-N-acetylanthranilic acid in 33% yield,m.p.67-8°. This compound was found to denitrosate readily giving the starting amide.

N-Nitroso-N-acetylanthranilic acid. - N-Acetylanthranilic acid was nitrosated using the method described above for o-t-butyl-N-nitrosoacetanilide to give N-nitroso-N-acetylanthranilic acid, m.p. ca. 70°. An accurate melting point could not be obtained since the compound denitrosated readily and was never prepared free from starting amide.

C Other Acylarylnitrosamines

The following acylarylnitrosamines were prep-

ared as described by Hey et al.[57] :

N-Nitrosoformanilide. - (80% Yield),

m.p.45° (decomp.), (lit.,[57] 45-6,decomp.).

N-Nitrosopropionanilide. - (81% Yield),

m.p.53° (decomp.), (lit.,[57] 53°, decomp.).

N-Nitrosoisobutyranilide. - (80% Yield),

m.p.34-5° (decomp.), (lit.,[57] 35°, decomp.).

IX PREPARATION OF ARYLAZOTRIARYLMETHANES

A p-Nitrophenylazotriphenylmethane

A solution of triphenylmethyl chloride (9.7g) was added to a solution of p-nitrophenylhydrazine (10.75g) in anhydrous ether at room temperature. The mixture was heated under reflux for 1.5 hr, allowed to stand for 12 hr at room temperature,filtered, and the filtrate added to a solution of potassium ferricyanide (54g) in water (200 ml). To the ice-cold solution was added sodium hydroxide solution (5.5g in 70ml water) with stirring, keeping the temperature at 0°. Stirring was continued for 1 hr, ether was added to give 500 ml of ethereal solution, and the solution washed with water (4 x 500 ml), dried, and the ether evaporated to give a yellow solid which was taken up in chloroform (20 ml) and reprecipitated with methanol (20 ml) to give p-nitrophenylazotriphenylmethane (4.0g,

30%), m.p.118-9°, (lit.,[152] 118.5°).

B Phenylazotriphenylmethane

Phenylazotriphenylmethane was prepared similarly as described by Gomberg[153] in 45% yield, m.p.110-11°, (lit.,[153] 111°).

X PREPARATION OF DIAZONIUM SALTS

A Benzenediazonium Chloride

Aniline hydrochloride was diazotised with pentyl nitrite in ethanol as described by Vogel[116] to give benzenediazonium chloride, m.p. (detonation), 101°. I.r. Nujol): 2300cm^{-1} (diazonium group).

B m-Nitrobenzenediazonium Chloride

m-Nitrobenzenediazonium chloride was prepared similarly. The dry solid was quickly reacted for fear of detonation.

I.r. (Nujol): 2300cm^{-1} (diazonium group).

C Benzenediazonium Bromide

Benzenediazonium Perbromide. - Phenylhydrazine (12g) was brominated as described by Chattaway[154] to give benzenediazonium perbromide (16.2g, 77%).

I.r. (Nujol): No absorption at 3300cm^{-1}(N-H in amine).

Benzenediazonium Bromide. - Benzenediazonium perbromide (3.45g) was converted to the diazonium bromide by reaction with phenylhydrazine (0.54g)

as described by Chattaway[155] . The benzenediazonium bromide was dried over phosphorus pentoxide at 0.05 mm and had m.p.(detonation),112°, (lit.,[155] 109°).

I.r. (Nujol): 2290cm^{-1} (diazonium group).

D m-Nitrobenzenediazonium Fluoroborate

This compound was described before. Benzenediazonium fluoroborate, prepared similarly, had m.p. (decomp.) 119-20°, (lit.,[116] 119-20°).

XI REACTIONS OF ACYLARYLNITROSAMINES WITH HALOGENOMETHANES

All reactions of acylarylnitrosamines, arylazotriarylmethanes, arynes and diazonium salts were carried out in an atmosphere of dry, oxygen-free nitrogen. In general, structural assignments based solely on g.l.c. retention times were the result of analysis on at least two different stationary phases. In all cases, the relation of a peak in the chromatogram to a particular compound required that the peak be enhanced, relative to other peaks, when authentic material was added to the reaction mixture. Where a temperature range is quoted in the g.l.c. conditions, the programming rate was 8°/min, and the programme commenced after the lower boiling products were eluted. The yields of decomposition products are quoted in moles per 100 moles of starting material, i.e., m/100m.

Literature values of physical constants quoted for authentic specimens prepared in preceding sections are not repeated in this section.

A Rections of N-nitrosoacetanilide

1. Decomposition in bromoform

The nitrosamide (1.02g, 6.2 mmoles) was allowed to decompose in bromoform (57.50g, 0.23 moles) at

50° for 24 hr. The cooled solution was examined by g.l.c. using the 1520B instrument (10% PEGA/60-120°; 10% SIL/106°) using toluene as marker and gave: benzene (1.8 m/100m), methylene bromide (1.7), bromobenzene (39.0), and phenyl acetate (10.0).
A parallel experiment gave: benzene (2.1), methylene bromide (1.7), bromobenzene (43.0), and phenyl acetate (10.0).

2. Decomposition in methylene bromide

The nitrosamide (1.06g, 6.5 mmoles) was allowed to decompose in methylene bromide (56.00g, 0.32 moles) at 50° for 24 hr. G.l.c. analysis as above using toluene as marker gave: benzene (10.6 m/100m), bromobenzene (45.2), bromoform (5.4) and phenyl acetate (6.7). A parallel experiment gave: benzene (10.5), bromobenzene (45.3), bromoform (5.2),and phenyl acetate (7.2).

3. Decomposition in methylene chloride

The nitrosamide (1.06g, 6.5 mmoles) was allowed to decompose in methylene chloride (14.90g, 0.18 moles) at 40° for 12 hr. Analysis by g.l.c. (10% SIL/109-120°; 3% QF1/40-120°) using toluene as marker gave: benzene (18.0 m/100m), chlorobenzene (19.7), and phenyl acetate (20.0). A parallel experiment gave; benzene (21.4), chlorobenzene (23.6) and phenyl acetate (16.2).

TABLE 1

Reactions of N-nitrosoacetanilide with halogenomethanes

Product	Yield (m/100 m of nitrosamide)		
	Reaction A.1. ($CHBr_3$)	A.2. (CH_2Br_2)	A.3. (CH_2Cl_2)
Benzene	1.8(2.1)	10.6(10.5)	18.0(21.4)
Chlorobenzene	-	-	19.7(23.6)
Bromobenzene	39.0(43.0)	45.2(45.3)	-
Phenyl acetate	10.0(10.0)	6.7(7.2)	20.0(16.2)
Bromoform	-	5.4(5.2)	-
Methylene bromide	1.7(1.7)	-	-

Figures in parentheses are the results of parallel reactions.

4(i) Decomposition in bromotrichloromethane at 15°

The nitrosamide (2.18g, 13.3 mmoles) was allowed to decompose in bromotrichloromethane (64.85g, 0.33 moles) at 15° for 12 hr. The precipitated diazonium salt was filtered, washed with a little bromotrichloromethane, and dried. G.l.c. examination of the filtrate (10% PEGA/ 60-120°; 10% SIL/90-140°) using bromoform as marker gave: chlorobenzene (1.3m/100m), bromobenzene (13.0), and phenyl acetate (14.8). The dry diazonium salt was allowed to decompose in fresh bromotrichloromethane (28.80g, 0.15 moles) at 50° for 12 hr and the solution analysed by g.l.c. as above to give: chlorobenzene (15.8 m/100m nitrosamide), bromobenzene (3.1), and phenyl acetate (6.0).

4(ii) Decomposition in bromotrichloromethane at 50°.

The nitrosamide (0.96g, 5.9 mmoles) was allowed to decompose in bromotrichloromethane (32.44g, 0.16 moles) at 50° for 12 hr. The solution was analysed using bromoform as marker to give: chlorobenzene (14.6 m/100m). bromobenzene (22.9), and phenyl acetate (16.0).
A parallel experiment gave: chlorobenzene (11.2), bromobenzene (19.0), and phenyl acetate (14.1).

5 The composition of the diazonium salt from 4(i).

N-Nitrosoacetanilide (2.39g, 14.6 mmoles) was allowed to decompose in bromotrichloromethane (63.48g,

0.32 moles) at 18°. After a few minutes a precipitate began to form and after 12 hr this was filtered, washed with some bromotrichloromethane and dried.

I.r. (Nujol): 1720 (C=O) and 2300cm^{-1}(diazonium group).

With alkaline β-naphthol, the dye benzeneazo-β-naphthol m.p. and mixed m.p.132°, was formed.

The dry diazonium salt was dissolved in water (74.97g) and a sample of this solution gave a positive test with silver nitrate, indicating the presence of halide, but the precipitated silver halide was soluble in dilute ammonia (silver bromide is not).

A test for bromide using sodium hypochlorite gave a negative result, (0.2% would have been detected).

Quantitative analysis for chloride using (a) Mohr's method and (b) Volhard's method indicated that the precipitate contained (a) 79.4% and (b) 78.4% of benzenediazonium chloride.

Decomposition of the diazonium salt in fresh bromotrichloromethane has been shown to give phenyl acetate (6.0 m/100m), and the i.r. spectrum contained an acetate carbonyl absorption, indicating the possibility of benzenediazonium acetate forming the remainder (ca. 21%) of the precipitate.

6(i). **Reaction with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane at 15°**

The nitrosamide (1.90g, 11.6 mmoles) was allowed to decompose in bromotrichloromathane (59.59g, 0.30moles) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (9.36g, 24.4 mmoles) at 15° for 15 hr. The solution was filtered and the filtrate examined by g.l.c. (10% PEGA/ 60-120°; 10% SIL/100°) using bromoform as marker to give: chlorobenzene (4.2 m/100m), bromobenzene (28.0), and phenyl acetate (17.0). The bulk of the reaction mixture was chromatographed on alumina (1000g). Elution with petrol/benzene (9:1) gave, after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.71g, 14 m/100m), m.p. and mixed m.p.199-200°. The i.r. and n.m.r. spectra were identical to those of the authentic specimen. 2,3,4,5-Tetraphenylcyclopentadienone was eluted in benzene.

A sample of the diazonium salt (0.63g) from a separate experiment with N-nitrosoacetanilide and bromotrichloromethane at 15°, was allowed to decompose in fresh bromotrichloromethane (36.18g, 0.18 moles) containing 2,3,4,5-tetraphenylcyclopentadienone.(4.86g, 12.7 mmoles) at 50° for 12 hr followed by heating under

reflux for 3 hr. Analysis of a small portion of the solution by g.l.c. (10% PEGA/60-120°; 10% SIL/90-140°) using bromoform as marker gave, after correction: chlorobenzene (9.6 m/100m nitrosamide), bromobenzene(7.2), and phenyl acetate (8.2). The bulk of the solution was chromatographed on alumina (100g); elution with benzene/petrol (1:9) gave, after recrystallisation from acetic acid, corrected: 1,2,3,4-tetraphenylnaphthalene (0.076g, 2.4 m/100m nitrosamide). Unreacted 2,3,4,5-tetraphenylcyclopentadienone was eluted in benzene.

6(ii). Reaction with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane at 50°

The nitrosamide (1.90g, 11.6 mmoles) was allowed to decompose in bromotrichloromethane (67.50g, 0.34 mmoles) containing 2,3,4,5-tetraphenylcyclopentadienone (9.50g, 24.7 mmoles) at 50° for 15 hr. Analysis of a small sample of the solution by g.l.c. (10% PEGA/60-120°; 10% SIL/100°) using bromoform as marker gave: chlorobenzene (4.8 m/100m), bromobenzene (22.3) and phenyl acetate (22.3). The bulk of the solution was chromatographed as above to give 1,2,3,4-tetraphenylnaphthalene (1.24g, 25.0 m/100m), m.p. and mixed m.p.199-200°. The i.r. spectrum was indistinguishable from that of the authentic.

TABLE 2

Reactions of N-nitrosoacetanilide with bromotrichloromethane

Product	Yield (m/100m of nitrosamide)					
	no aryne trap			with aryne trap		
Reaction	A4(i) 15°		A4(ii) 50°	A6(i) 15°		A6(ii) 50°
Chlorobenzene	1.3	15.8	14.6(11.2)	4.2	9.6	4.8
Bromobenzene	13.0	3.1	22.9(19.0)	28.0	7.2	22.3
Phenyl Acetate	14.8	6.0	16.0(14.1)	17.0	8.2	22.3
1,2,3,4-Tetraphenylnaphthalene			-	14.0	2.4	25.0

Figures in the first column of A4(i) and A6(i) represent yields from the decomposition of N-nitrosoacetanilide at 15°; figures in the second columns represent the yields (m/100m nitrosamide) from the decomposition of the intermediate diazonium salt in fresh bromotrichloromethane and bromotrichloromethane admixed with 2,3,4,5-tetraphenylcyclopentadienone respectively. Figures in parentheses represent results of parallel reactions.

B Reactions of p-nitro-N-nitrosoacetanilide

1. Decomposition in bromotrichloromethane

The nitrosamide (2.74g, 13.1 mmoles) was allowed to decompose in bromotrichloromethane (48.40g, 0.24 moles) at 50° for 12 hr. The solution was analysed by g.l.c. (10% PEGA/90-140°; 10% SIL/140-180°) using p-dibromobenzene as marker and gave: p-dichlorobenzene (0.8 m/100m), p-bromochlorobenzene (2.5), p-chlorophenyl acetate (2.0), p-chloronitrobenzene (8.0), p-bromophenyl acetate (4.0), p-bromonitrobenzene (31.0), and p-nitrophenyl acetate (3.4).

2. Decomposition in methylene bromide

The nitrosamide (1.18g, 5.64 mmoles) was allowed to decompose in methylene bromide (22.31g, 0.128 moles) at 50° for 24 hr. Analysis by g.l.c. (10% PEGA/90-150°; 10% SIL/90-160°) using p-dibromobenzene as marker gave: nitrobenzene (8.3 m/100m), p-nitrobromobenzene (43.0), phenyl acetate (0.9), and p-bromophenyl acetate (2.9). p-Nitrophenyl acetate was not detected, (0.1 m/100m would have been seen).

C Decomposition of p-methoxy-N-nitrosoacetanilide in methylene bromide

The nitrosamide (0.76g, 3.9 mmoles) was allowed to decompose in methylene bromide (18.0g, 0.10 moles)

TABLE 3

Reactions of p-nitro-N-nitrosoacetanilide with halogenomethanes

Product	Yield (m/100m of nitrosamide)	
Reaction	B1	B2
	$BrCCl_3$	CH_2Br_2
p-Dichlorobenzene	0.8	-
p-Bromochlorobenzene	2.5	-
p-Chlorophenyl acetate	2.0	-
p-Bromophenyl acetate	4.0	2.9
p-Nitrochlorobenzene	8.0	-
p-Nitrobromobenzene	31.0	43.0
p-Nitrophenyl acetate	3.4	0
Nitrobenzene	0	8.3
Phenyl acetate	0	0.9

at 50° for 24 hr. Analysis by g.l.c. (10% PEGA/65-115°; 10% SIL/115-170°) using nitrobenzene as marker gave: bromoform (0.9 m/100m), anisole (9.8), and p-bromoanisole (30.2). p-Methoxyphenyl acetate (0.1 m/100m would have been detected) was absent.

D Decomposition of p-carbethoxy-N-nitrosoacetanilide in methylene bromide

The nitrosamide (0.92g, 3.9 mmoles) was allowed to decompose in methylene bromide (19.2g, 0.11 moles) at 50° for 12 hr. G.l.c. analysis (2% NPGS/105-170°; 3% QF1/105-170°) using p-dichlorobenzene as marker gave: ethyl benzoate (11.4 m/100m), ethyl p-bromobenzoate (68.8), p-carbethoxyphenyl acetate (16.7).

A parallel experiment gave: ethyl benzoate (7.92), ethyl p-bromobenzoate (50.8) and p-carbethoxyphenyl acetate (12.8).

E Decomposition of N-nitrosoformanilide in methylene bromide

The nitrosamide (1.43g, 9.5 mmoles) was allowed to decompose in methylene bromide (44.08g, 0.25 moles) at 50° for 12 hr. Analysis of the solution by g.l.c. using toluene as marker gave: benzene (8.2 m/100m), bromobenzene (41.7), and phenyl formate (0.7).

A parallel experiment gave: benzene (7.1), bromobenzene (39.7) and phenyl formate (0.9).

F Decomposition of N-nitrosopropionanilide in methylene bromide

The nitrosamide (1.59g, 8.9 mmoles) was allowed to decompose in methylene bromide (54.89g, 0.32 moles) at 50° for 12 hr. G.l.c. analysis (10% PEGA/60-100°; 10% SIL/80-120°) using toluene as marker gave: benzene

(12.4 m/100m), bromobenzene (67.5), and phenyl propionate (1.8). A parallel experiment gave: benzene (11.0), bromobenzene (66.0), and phenyl propionate (1.8).

G Decomposition of N-nitrosoisobutyranilide in methylene bromide

The nitrosamide (0.22g, 1.2 mmoles) was allowed to decompose in methylene bromide (5.44g, 0.03 moles) at 50° for 12 hr. The mixture was shown by g.l.c. (10% PEGA/60-120°;10% SIL/80-100° to contain: benzene (11.8 m/100m), bromobenzene (64.5), and phenyl isobutyrate (0.9).

H Reactions of o-t-butyl-N-nitrosoacetanilide

1. Decomposition in bromotrichloromethane

o-t-Butyl-N-nitrosoacetanilide (1.83g, 8.3 mmoles) was allowed to decompose in bromotrichloromethane (40.35g, 0.20 moles) at room temperature for 36 hr then heated slowly to reflux temperature to complete the decomposition. The solution was analysed by g.l.c. (10% SIL/180° for analysis, 2% NPGS capillary and 5% XP/125° for isomer ratio) using p-dichlorobenzene as marker and gave: o-t-butylchlorobenzene (23.0 m/100m), m-t-butylchlorobenzene (2.0), o-t-butylbromobenzene (4.0), m-t-butylbromobenzene (0.9), o-t-butylphenyl acetate (45.0), and m-t-butylphenyl acetate (16.5).

2. Decomposition in methylene bromide

The nitrosamide (1.04g, 4.73 mmoles) was allowed

to decompose in methylene bromide (19.83g, 0.11 moles) at room temperature for 36 hr then heated slowly to reflux temperature to complete the reaction. Analysis by g.l.c. as above gave: t-butylbenzene (2.5 m/100m), o-t-butylbromobenzene (14.0), m-t-butylbromobenzene (2.5), o-t-butylphenyl acetate (42.0), and m-t-butylphenyl acetate (21.0).

3. Decomposition in bromotrichloromethane in the presence of furan

o-t-Butyl-N-nitrosoacetanilide (4.79g, 21.4 mmoles) was allowed to decompose in a mixture of furan (17.16g, 0.25 moles) and bromotrichloromethane (50.96g, 0.26 moles) at room temperature for 36 hr then heated slowly to reflux temperature to complete the reaction A small portion of the mixture was analysed by g.l.c. (conditions as in H1) to give: o-t-butylchlorobenzene (9.0 m/100m), m-t-butylchlorobenzene (0), o-t-butylbromobenzene (14.0), m-t-butylbromobenzene (0), o-t-butylphenyl acetate (47.0), and m-t-butylphenyl acetate (0). A separate analysis on 2% NPGS gave the ratio of an unknown compound to the p-dichlorobenzene marker.

The bulk of the reaction mixture was distilled to give the following fractions: (a) 18.16g, colourless liquid, b.p.32-64°; (b) 12.40g, colourless liquid,

b.p.64-80°; (c) 14.51g, colourless liquid, b.p.40-58°/40 mm; (d) 0.14g, yellow liquid, b.p.30-65°/0.1 mm; (e) 1.58g, yellow liquid, b.p.65-6°/0.1 mm; (f) 11.62g, yellow oil, b.p.67-120°/0.1 mm; (g) black residue, 0.59g, remained in the distillation flask.

Fractions (f) and (g) were shown by g.l.c. (2% NPGS/120°) to contain o-t-butylphenyl acetate and 5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide by peak enhancement with authentic samples. These compounds were separated by preparative g.l.c. (7 ft x 0.375 in 10% PEGA column at 98°) to give pure o-t-butylphenyl acetate (i.r. and b.p. identical to those of the authentic) and 5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide, m.p. and mixed m.p. 56-7°.

(Found: C, 83.75; H, 8.21. $C_{14}H_{16}O$ requires C, 84.0; H, 8.0%).

I.r. (melt): 1375 and 1365 (t-butyl); 1125 (C-O-C) and 715cm^{-1}(cis CH=CH).

N.m.r. ($CDCl_3$): τ 2.80-3.20(complex, aromatic and olefinic, 5H) 3.88 and 4.38 (bridgehead, 2H) and 8.65 (t-butyl).

After calibration of the 1520B with the authentic sample, the yield of 5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide was computed as (20.0 m/100m).

TABLE 4

Reactions of acylarylnitrosamines with methylene bromide

Acylarylnitrosamine $R'C_6H_4N(NO)COR''$		Product yield (m/100m of nitrosamide)				
R'	R''	C_6H_5R'	$R'C_6H_4Br$	$R'C_6H_4OCOR''$	$CHBr_3$	$\frac{ArBr}{ArH}$
H	H	8.2(7.1)	41.7(39.7)	0.7(0.9)	0	5.1(5.6)
H	CH_3	10.6(10.5)	45.2(45.3)	6.7(7.2)	5.4(5.2)	4.3(4.3)
H	C_2H_5	12.4(11.0)	67.5(66.0)	1.8(1.8)	0	5.5(6.0)
H	$C_3H_7^i$	11.8	64.5	0.9	0	5.5
*p-NO_2	CH_3	8.3	43.0	0	0	5.2
p-OCH_3	CH_3	9.8	30.2	0	0.9	3.1
p-COOEt	CH_3	11.4(7.92)	68.8(50.8)	16.7(12.8)	0	6.0(6.4)
‡o-Bu^t	CH_3	2.5	14.0	42.0	0	5.6

* Phenyl acetate (0.9) and p-bromophenyl acetate (2.9) were also present.

‡ m-t-Butylbromobenzene (2.5) and m-t-butylphenyl acetate(21.0) were also present.

Figures in parentheses represent results of parallel reactions.

TABLE 5

Reactions of o-t-butyl-N-nitrosoacetanilide with halogenomethanes

Product	Yield (m/100m of nitrosamide)		
Reaction	H1	H2	H3
	$BrCCl_3$	CH_2Br_2	$BrCCl_3$/furan
t-Butylbenzene	-	2.5	-
o-t-Butylchlorobenzene	23.0	-	9.0
m-t-Butylchlorobenzene	2.0	-	0
o-t-Butylbromobenzene	4.0	14.0	14.0
m-t-Butylbromobenzene	0.9	2.5	0
o-t-Butylphenyl acetate	45.0	42.0	47.0
m-t-Butylphenyl acetate	16.5	21.0	0
5-t-Butyl-1,4-dihydronaphthalene-1,4-endoxide			20.0

I Reactions of m-bromo-N-nitrosoacetanilide

1. Decomposition in bromotrichloromethane

m-Bromo-N-nitrosoacetanilide (0.62g, 2.6 mmoles) was allowed to decompose in bromotrichloromethane (9.96g, 0.05 moles), at 50° for 12 hr. Analysis by g.l.c. (10% PEGA/100-170°; 10% SIL/170°) using m-dichlorobenzene as

marker gave: m-chlorobromobenzene (18.2 m/100m), m-dibromobenzene (39.0), and m-bromophenyl acetate (11.2). A parallel experiment gave: m-chlorobromobenzene (19.8 m/100m), m-dibromobenzene (38.8), and m-bromophenyl acetate (9.5).

2. Decomposition in bromotrichloromethane in the presence of 2,3,4,5-tetraphenylcyclopentadienone

m-Bromo-N-nitrosoacetanilide (1.60g 6.6 mmoles) was allowed to decompose in bromotrichloromethane (35.53g, 0.18 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (4.33g, 11.3 mmoles) at 50° for 12 hr. Analysis of a small portion of the solution (g.l.c. conditions and marker as in 1) gave: m-chlorobromobenzene (12.2 m/100m), m-dibromobenzene (43.2) and m-bromophenyl acetate (4.5). The bulk of the solution was chromatographed on alumina (200g) to give, on eluting with benzene/petrol (1:9) a yellow-red solid. (0.85g). This was recrystallised from acetic acid to give 5-bromo-1,2,3,4-tetraphenylnaphthalene (0.79g, 23.4 m/100m), m.p. and mixed m.p. 233-4°, (lit.,[66] 234-5°).

(Found : C, 79.40; H, 4.53. $C_{34}H_{23}Br$ requires C, 79.80; H, 4.50%).

The i.r. spectrum was identical to that of the authentic sample provided by Dr.J.B.Thomson. 2,3,4,5-Tetraphenyl-

cyclopentadienone (0.25g) was eluted in benzene and a black tar (0.35g) in methanol.

J. Attempts to trap dichlorocarbene in the reactions of N-nitrosoacetanilide

1. Reaction with α-methylstyrene in carbon tetrachloride

N-Nitrosoacetanilide (0.19g, 1.2 mmoles) was allowed to decompose in carbon tetrachloride (3.11g, 20.3 mmoles) in the presence of "galvinoxyl" (0.055g, 0.13 mmoles) and α-methylstyrene (1.14g, 9.7 mmoles) at room temperature for 48 hr followed by heating to reflux temperature for 2 hr. G.l.c. (10% PEGA/95-165°; 10% SIL/90-160°) showed no 1,1-dichloro-2-methyl-2-phenylcyclopropane. (0.1 m/100m would have been detected).

2. Reaction with cyclohexene in carbon tetrachloride

N-Nitrosoacetanilide (1.53g, 9.3 mmoles) was allowed to decompose in carbon tetrachloride (20.48g, 0.13 moles) containing cyclohexene (2.53g, 30.8 mmoles) and t-butylcatechol (0.10g, 0.6 mmoles) at room temperature followed by heating to reflux temperature for 2 hr. G.l.c. (10% SIL/86°) showed chlorobenzene, bicyclohex-2-enyl and phenyl acetate but no dichloronorcarane. (0.1 m/100m would have been detected).

3. Reaction with α-methylstyrene in bromotrichloromethane

N-Nitrosoacetanilide (0.22g, 1.34 mmoles) was all-

TABLE 6

Reactions of m-bromo-N-nitrosoacetanilide with halogenomethanes

Product	Yield (m/100m of nitrosamide)	
Reaction	I1	I2
	$BrCCl_3$	$BrCCl_3$ + trap
m-Chlorobromobenzene	18.2(19.8)	12.2
m-Dibromobenzene	39.0(38.8)	43.2
m-Bromophenyl acetate	11.2(9.5)	4.5
5-Bromo-1,2,3,4-tetraphenylnaphthalene		23.4

Figures in parentheses represent results of parallel reactions

owed to decompose in bromotrichloromethane (8.19g, 41.4 mmoles) containing 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxide (0.18g, 1.1 mmoles) and α-methylstyrene (0.80g, 6.83 mmoles) at room temperature for 65 hr followed by heating under reflux for 2 hr. G.l.c. examination (10% PEGA/95-150°) showed no 1,1-dichloro-2-methyl-2-phenylcyclopropane. (0.1 m/100m would have been detected).

K Other reactions of acylarylnitrosamines with halogenomethanes

1. Reaction of N-nitrosoacetanilide with tetrachloroethane

N-Nitrosoacetanilide (9.58g, 0.06 moles) was allowed to decompose in tetrachloroethane (250.86g, 1.60 moles) at room temperature for 48 hr followed by heating under reflux for 2 hr. G.l.c. analysis (2% NPGS/ 60-120°) indicated the presence of benzene, chlorobenzene and phenyl acetate. No α, β, β - trichloroethylacetate was observed.

2. Reaction of N-nitrosoacetanilide with methylene bromide

A concentrated solution of N-nitrosoacetanilide in methylene bromide at 15° was allowed to stand for 2 hr and the brown precipitate filtered, and washed with ether.

I.r. (Nujol) : 2300 cm^{-1}(diazonium group). The spectrum was very similar to that of benzenediazonium bromide.

3. Reaction of N-nitrosoacetanilide with bromoform

A concentrated solution of N-nitrosoacetanilide in bromoform at 15° was allowed to stand as above, and the precipitate filtered and washed with ether.

I.r. (Nujol) : 2300 cm^{-1} (diazonium group). The spectrum was indistinguishable from that of benzenediazonium bromide.

4. Reaction of N-nitrosoacetanilide with methylene chloride

A concentrated solution of N-nitrosoacetanilide in methylene chloride was allowed to stand at 15° for 2 hr and the precipitate filtered, washed with a little methylene chloride and dried.

I.r. (Nujol) : 2300 cm^{-1} (diazonium group). The spectrum was indistinguishable from that of benzenediazonium chloride.

5. Reaction of 4-chloro-N-nitrosobenzanilide with carbon tetrachloride

The nitrosamide (1.83g, 7.0 mmoles), m.p. (decomp.) 76°, lit.,[66] 75°, was allowed to decompose in carbon tetrachloride (42.54g, 0.27 moles) at room temperature for 12 hr. The precipitate (0.91g) was filtered, washed with a little fresh solvent and dried.

I.r. (Nujol) : 3000 (broad, OH), 2280 (diazonium group), 1680 cm^{-1} (broad, C=O).

Halogen analysis, as described before, indicated that the precipitate contained 16% benzenediazonium chloride, the remainder being a mixture of benzenediazonium p-chlorobenzoate and p-chlorobenzoic acid. Analysis of the filtrate by g.l.c. (2% NPGS/75-180°; 3% QF1/ 75-180°) using p-dichlorobenzene as marker gave: chlorobenzene (17.0 m/100m). Subsequent decomposition

of a portion of the precipitated diazonium salt in fresh carbon tetrachloride gave after g.l.c. analysis as above : chlorobenzene (13.0 m/100m), phenyl 4-chlorobenzoate (0.1). p-Chlorobenzoic acid (0.25) was filtered from the reaction mixture.

A parallel reaction in which the precipitate was filtered after 30 min showed a lower percentage of benzenediazonium chloride (9.3%) in the precipitate. A broad absorption in the i.r. spectrum at 3000 cm^{-1} indicated the presence of p-chlorobenzoic acid.

XII REACTIONS OF ARYLAZOTRIARYMETHANES WITH HALOGENOMETHANES

A Reactions of phenylazotriphenylmethane

1. Decomposition in bromoform

Phenylazotriphenylmethane (0.85g, 2.5 mmoles) was allowed to decompose in bromoform (17.00g, 0.067 moles) at 50° for 15 hr. Analysis by g.l.c. using the 1520B with toluene as marker (10% PEGA/50-100°; 10%SIL/75-120°) gave: benzene (4.1 m/100m), methylene bromide (31.0), and bromobenzene (63.0). A parallel experiment gave: benzene (3.8), methylene bromide (23.0), and bromobenzene (52.0).

2. Decomposition in methylene bromide

Phenylazotriphenylmethane (0.89g, 2.7 mmoles) was allowed to decompose in methylene bromide (14.5g, 0.083 moles) at 50° for 15 hr. Analysis using toluene as marker and the above g.l.c. conditions gave: benzene (24.0 m/100m), and bromobenzene (24.0). A parallel experiment gave: benzene (23.0), and bromobenzene (19.0).

3. Decomposition in methylene chloride

Phenylazotriphenylmethane (0.49g, 1.47 mmoles) was heated in a Carius tube with methylene chloride (26.72g, 0.31 moles) at 50° for 4 days to ensure complete decomposition. The solution was analysed by g.l.c.

(10% SIL/80°; 3% QF1/28°) using toluene as marker and gave: benzene (72.4 m/100m). Chlorobenzene (0.1 m/100m would have been detected) was absent.

B Reaction of p-nitrophenylazotriphenylmethane with bromotrichloromethane

p-Nitrophenylazotriphenylmethane (0.90g, 2.4 mmoles) was allowed to decompose in bromotrichloromethane (12.05g, 0.067 moles) at 50° for 24 hr. The solution was analysed by g.l.c. (10% PEGA/150-170°;10 SIL/180°) using p-dibromobenzene as marker and gave: p-bromonitrobenzene (69.0 m/100m). p-Nitrochlorobenzene (0.1 m/100m would have been detected) was absent).

XIII REACTIONS OF DIAZONIUM SALTS WITH HALOGENOMETHANES

A Reactions of benzenediazonium chloride

1. Decomposition in methylene bromide

Benzenediazonium chloride (1.31g, 9.3 mmoles) was allowed to decompose in methylene bromide (21.25g, 0.12 moles) at 50° for 2 days. G.l.c. analysis (10% PEGA/50-100°; 10% SIL/65-120°) using p-dibromobenzene as marker gave: benzene (2.0 m/100m), chlorobenzene (25.0), and bromobenzene (19.0).

2. Decomposition in chloroform

Benzenediazonium chloride was allowed to decompose in chloroform (16.61g, 0.14 moles) at 50° for 48 hr.

TABLE 7

Reactions of arylazotriarylmethanes with halogenomethanes

Arylazotriphenylmethane $RC_6H_4N{=}NCPh_3$ R	Solvent	Product yield (m/100m of source) C_6H_5R	RC_6H_4Br	RC_6H_4Cl	CH_2Br_2
H	$CHBr_3$	4.1(3.8)	63.0(52.0)	-	31.0(23.0)
H	CH_2Br_2	24.0(23.0)	24.0(19.0)	-	-
H	CH_2Cl_2	72.4	-	0	-
NO_2	$BrCCl_3$	-	69.0	0	-

Figures in parentheses represent results of parallel reactions.

Analysis by g.l.c. as above gave: benzene (7.8 m/100m), and chlorobenzene (28.5).

3. Reaction of benzenediazonium chloride with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane

Benzenediazonium chloride (1.06g, 7.6 mmoles) was allowed to decompose in bromotrichloromethane (19.15g, 0.097 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (2.37g, 6.2 mmoles) at 50° for 16 hr, and then heated under reflux for 2 hr. Analysis of a small portion of the solution (10% PEGA/60-120°; 10% SIL/ 90-120°) using bromoform as marker gave: chlorobenzene (37.0 m/100m), and bromobenzene (11.0). The bulk of the solution

was then chromatographed on alumina (100g) to give, eluting with benzene/petrol (1:9), after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.18g, 5.4 m/100m), m.p. and mixed m.p.199-200°.The i.r. spectrum was identical to that of the authentic. 2,3,4,5-Tetraphenylcyclopentadienone was eluted in benzene, and a black tar (0.55g) in methanol.

B Reaction of benzenediazonium bromide with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane

Benzenediazonium bromide (0.95g, 5.1 mmoles) was allowed to decompose in bromotrichloromethane (34.17g, 0.17 moles) in the presence of 2,3,4,5-tetraphenylcyclopentadienone (1.76g, 4.6 mmoles) at 50° for 2 days. A portion of the solution was analysed by g.l.c. (10% PEGA/60-120°; 10% SIL/100°) using bromoform as marker and gave: chlorobenzene (3.3 m/100m) and bromobenzene (68.2). The bulk of the solution was chromatographed on alumina (100g) and elution with benzene/petrol (1:9)gave, after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.02g, 0.9 m/100m), m.p.and mixed m.p. 199-200°; i.r. was identical to that of the authentic.

C Reaction of benzenediazonium fluoroborate with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane

Benzenediazonium fluoroborate (1.76g, 9.2 mmoles)

was heated under reflux in bromotrichloromethane (56.47g, 0.29 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (5.12g, 13.3 mmoles) for 12 hr. A small portion of the solution was analysed by g.l.c. (10% SIL/ 76°; 10% PEGA/40°) using bromoform as marker to give: fluorobenzene (95.5 m/100m), chlorobenzene (2.4) and bromobenzene (<0.1). Chromatography on alumina afforded no 1,2,3,4-tetraphenylnaphthalene.

D Reaction of m-nitrobenzenediazonium fluoroborate with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane

m-Nitrobenzenediazonium fluoroborate (0.54g, 2.3 mmoles) was heated under reflux in bromotrichloromethane (24.30g, 0.12 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (3.02g, 7.9 mmoles) for 24 hr. Analysis of a small portion of the solution by g.l.c. as above gave: m-nitrofluorobenzene (40.0 m/100m), m-nitrobromobenzene (10.7), and m-nitrochlorobenzene (<0.1). Chromatography on alumina afforded no 5-nitro-1,2,3,4-tetraphenylnaphthalene. T.l.c. of the reaction mixture showed no spot with an R_f value equal to that of an authentic sample provided by Dr. J.B.Thomson.

E Reaction of m-nitrobenzenediazonium chloride with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane

m-Nitrobenzenediazonium chloride (0.73g, 3.9

mmoles) was heated under reflux in bromotrichloromethane (50.80g, 0.26 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (1.94g, 5.1 mmoles) for 24 hr. Analysis of a small portion of the solution by g.l.c. (10% PEGA/120-160°; 10% SIL/150-170°) using bromoform as marker gave: m-chloronitrobenzene (65.0 m/100m), and m-bromonitrobenzene (9.0). Chromatography on alumina afforded no 5-nitro-1,2,3,4-tetraphenylnaphthalene. T.l.c. of the reaction mixture showed no spot of R_f value equal to that of an authentic sample.

TABLE 8

Reactions of diazonium salts with halogenomethanes

A Reactions of benzenediazonium chloride

Product	Yield (m/100m of source)		
Reaction	A1 (CH_2Br_2)	A2 ($CHCl_3$)	A3 ($BrCCl_3$/TC)
Benzene	2.0	7.8	-
Chlorobenzene	25.0	28.5	37.0
Bromobenzene	19.0	-	11.0
1,2,3,4-Tetraphenylnaphthalene	-	-	5.4

In these tables, the abbreviation TC has been used for 2,3,4,5-tetraphenylcyclopentadienone.

B Reactions of benzenediazonium bromide

Product	Yield (m/100m of source) Reaction B ($BrCCl_3$/T.C.)
Bromobenzene	68.2
Chlorobenzene	3.3
1,2,3,4-Tetraphenylnaphthalene	0.9

C Reactions of benzenediazonium fluoroborate

Product	Yield (m/100m of source) Reaction C ($BrCCl_3$/T.C.)
Fluorobenzene	95.5
Bromobenzene	< 0.1
Chlorobenzene	2.4
1,2,3,4-Tetraphenylnaphthalene	0

TABLE 9

Reactions of m-nitrobenzenediazonium salts with halogeno-methanes

D Reactions of m-nitrobenzenediazonium fluoroborate

Product	Yield (m/100m of source) Reaction D ($BrCCl_3$/T.C.)
m-Nitrofluorobenzene	40.0
m-Nitrochlorobenzene	< 0.1
m-Nitrobromobenzene	10.7
5-Nitro-1,2,3,4-tetraphenylnaphthalene	0

E Reactions of m-nitrobenzenediazonium chloride

Product	Yield (m/100m of source) Reaction E ($BrCCl_3$/T.C.)
m-Nitrochlorobenzene	65.0
m-Nitrobromobenzene	9.0
5-Nitro-1,2,3,4-tetraphenylnaphthalene	0

XIV REACTIONS OF ACYLARYLNITROSAMINES WITH ARYNOPHILES

A Reactions of N-nitrosoacetanilide

1. Reaction with 2,3,4,5-tetraphenylcyclopentadienone in benzene

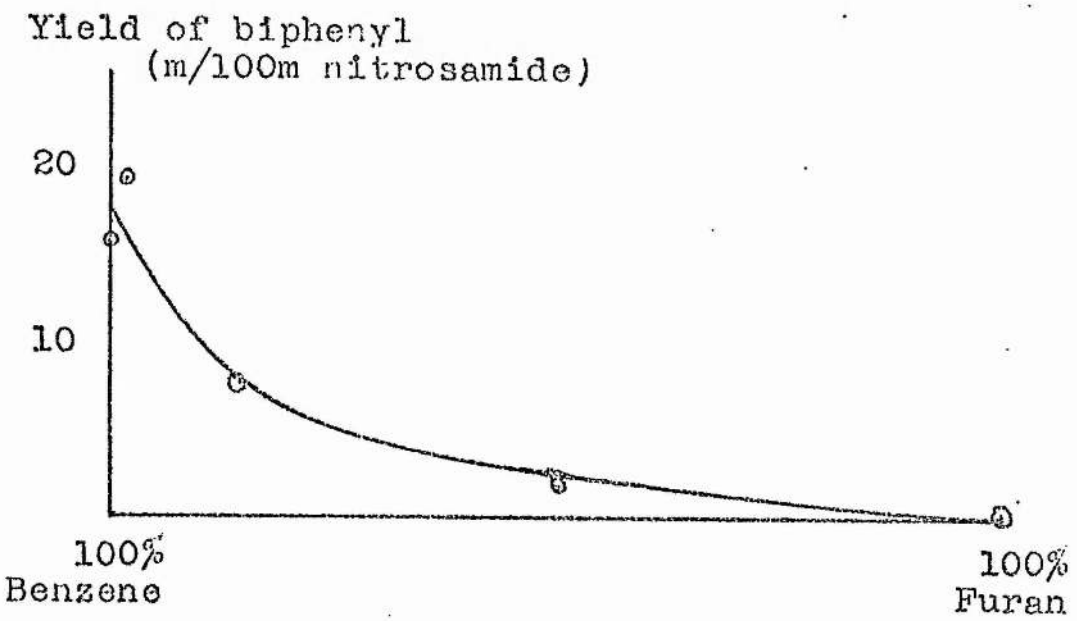
The nitrosamide (0.82g, 5.0 mmoles) was allowed to decompose in benzene (4.69g, 0.06 mmoles) containing 2,3,4,5-tetraphenylcyclopentadienone (3.84g, 10 mmoles) at room temperature for 24 hr, then heated slowly to reflux to complete the reaction. G.l.c. analysis of a small portion of solution (10% SIL/170°; 3% APL 130°) using the D.6. instrument with bibenzyl as internal standard gave: biphenyl (16.0 m/100m). Chromatography of the bulk of the solution on alumina (100g) gave, on eluting with benzene/petrol (1:9), after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.49g, 22.0 m/100m), m.p.and mixed m.p.199-200°. The i.r. spectrum was indistinguishable from that of the authentic.

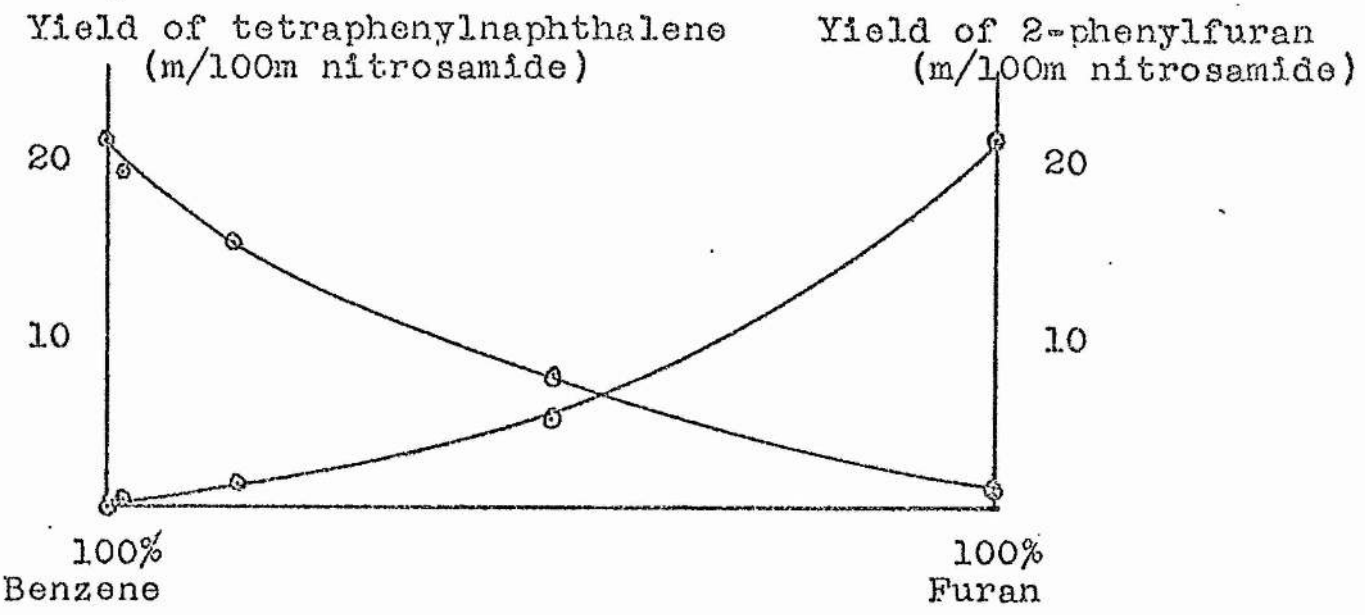
2. Reaction with 2,3,4,5-tetraphenylcyclopentadienone in furan

The nitrosamide (0.82g, 5.0 mmoles) was allowed to decompose in furan (4.08g, 0.06 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (3.84 g, 10.0 m moles) at room temperature for 24 hr then heated slowly to reflux temperature in order to complete the reaction. G.l.c. analysis as above gave: 2-phenylfuran (22.0m/100m).

Figure 1

Reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in mixtures of benzene and furan





Chromatography on alumina eluting with benzene/petrol (1:9) gave, after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.03g, 1.4 m/100m), m.p. and mixed m.p. 199-200°. The i.r. spectrum was indistinguishable from that of the authentic.

3. Reaction with 2,3,4,5-tetraphenylcyclopentadienone in mixtures of furan and benzene

Experiments were performed as described above (1 and 2). The reactants and products are tabulated below and are expressed graphically in figure 1.

TABLE 10

Reactants				Products		
N.N.A. mmoles	Benzene moles	Furan moles	T.C. mmoles	Biphenyl m/100m	2-Phenyl-furan m/100m	T.P.N. m/100m
5.0	0.06	0.01	10.0	7.5	2.3	15.0
5.0	0.06	0.06	10.0	3.0	4.7	7.5
5.0	0.06	0.001	10.0	18.0	0.1	18.0

The abbreviations used represent N-nitrosoacetanilide, 2,3,4,5-tetraphenylcyclopentadienone, and 1,2,3,4-tetraphenylnaphthalene respectively.

4. Reaction with 2,5-di-p-methoxyphenyl-3,4-diphenyl-cyclopentadienone

The nitrosamide (0.82g, 5.0 mmoles) was allowed

to decompose in benzene (7.8g, 0.1 moles) containing 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (2.22g, 5.0 mmoles) at room temperature for 24 hr, after which the mixture was heated slowly to reflux temperature. Chromatography on alumina (100g) on eluting with petrol gave, after recrystallisation from methanol, biphenyl (0.05g, 3.0 m/100m), m.p. and mixed m.p. 68-9°. Elution with benzene/petrol (1:9) gave, after recrystallisation from petrol (b.p. 60-80°), 1,4-di-p-methoxyphenyl-2,3-diphenylnaphthalene (1.81g, 82.0 m/100m), m.p. and mixed m.p. 223°. The i.r. and n.m.r. spectra were identical to those of the authentic.

5. Reaction with 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone

The nitrosamide (0.82g, 5 mmoles) was allowed to decompose in benzene (7.8g, 0.1 moles) containing 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone (2.06g, 5.0 mmoles) at room temperature for 24 hr then heated slowly to reflux temperature. Chromatography on alumina (100g) gave, on eluting with benzene/petrol (1:9), after recrystallisation from petrol (b.p.60-80°), 1,4-di-p-methylphenyl-2,3-diphenylnaphthalene (1.69g, 82.0 m/100m), m.p. and mixed m.p. 226°. The i.r. spectrum was identical to that of the authentic.

6. Reaction with 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone

The nitrosamide (0.25g, 1.5 mmoles) was allowed

to decompose in carbon tetrachloride (40.0g, 0.26 moles) containing 2,5-di-p-methylsulphonyphenyl-3,4-diphenyl-cyclopentadienone (0.83g, 1.5 mmoles) at 40° for 12 hr. (Carbon tetrachloride was chosen as solvent in this case because of difficulties experienced using benzene in which the arynophile was not very soluble). Unreacted arynophile was removed by heating the residue which remained after removal of the solvent, under reflux in chlorobenzene containing maleic anhydride (0.82g) for 12 hr. Chromatography on alumina (100g) eluting with benzene/chloroform (3:1) gave , after recrystallisation from acetic acid (twice) and petrol/benzene(1:1) (petrol b.p. 100-120°), 1,4-di-p-methylsulphonylphenyl-2,3-diphenylnaphthalene (0.16g, 19.0 m/100m); m.p. and mixed m.p. 339-40°. The i.r. spectrum was indistinguishable from that of the authentic.

7. Reaction with benzene

N-Nitrosoacetanilide (10.0g, 0.06 moles) was allowed to decompose in benzene (95.00g, 1.2 moles) at 50° for 12 hr. Chromatography on alumina eluting with benzene/petrol (1:9) gave biphenyl (4.03g, 43.0 m/100m), m.p. and mixed m.p. 68-9° after recrystallisation from methanol. A sample of the crude product was examined by n.m.r. ($CDCl_3$) but no absorptions at τ = 5.2 (bridgehead protons in benzobicyclo [2,2,2] octatriene[98]).

were detected. (0.2 m/100m would have been detected).

8. Reaction with anthracene

N-Nitrosoacetanilide (1.64g, 10.0 mmoles) was allowed to decompose in benzene (15.60g, 0.2 moles) containing anthracene (1.78g, 10.0 mmoles) at 50° for 12 hr then heated to reflux temperature. After removal of the solvent, excess anthracene was removed by heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (1.78g) for 10hr. Chromatography on alumina gave the following fractions on eluting with benzene/petrol (1:9) : (a) 0.12g, yellow solid, (b) 0.54g, yellow solid. Fraction (a) was recrystallised from methanol to give biphenyl (0.13g, 10 m/100m). Fraction (b) was shown by g.l.c. (10% PEGA/ 200°) to contain one major component. Preparative g.l.c. (2% NPGS/200°) using the D.6. instrument afforded a sample of this compound, which was identified as triptycene, (yield by g.l.c. using the isolated yield of biphenyl as internal standard, 5.0 m/100m), m.p. 251-2°. M^+ = 254. The i.r. and n.m.r. spetra were indistinguishable from those of the authentic.

By comparison of the g.l.c. chromatograms before and after workup, it was observed that the major product of the reaction was absent, after reaction with

maleic anhydride. From a parallel reaction , preparative g.l.c. (2% NPGS/200°) afforded a sample of this compound, which was identified as 9-phenylanthracene, (yield by g.l.c. 54.0 m/100m) m.p. and mixed m.p. 153-4°. The i.r. spectrum was indistinguishable from that of an authentic sample gifted by Professor R.O.C. Norman.

9. Reaction with 9,10-dimethylanthracene

N-Nitrosoacetanilide (3.28g, 20 mmoles) was containing 9,10-dimethylanthracene (16.48 g, 60.0 m moles) allowed to decompose in benzene (39.0g, 0.5 moles) at 50° for 12 hr. After removal of the benzene, unreacted 9,10-dimethylanthracene was removed by heating the residue under reflux in chlorobenzene (50 ml) containing maleic anhydride (16.5g). Chromatography on alumina (300g) eluting with benzene/petrol (1:9) gave, after recrystallisation from petrol (b.p. 60-80°), 9,10-dimethyltriptycene (1.60g, 30 m/100m), m.p. 328-30°, (lit.,[143] 329-330°).

(Found: C, 93.72; H, 6.52. $C_{22}H_{18}$ requires C, 93.62; H, 6.38%). M^+ = 282.

N.m.r. ($CDCl_3$): τ 2.45-3.20 (A_2B_2, 12 H) and 7.6 (s, CH_3 6 H).

10. Reaction with 9,10-dimethoxyanthracene

N-Nitrosoacetanilide (0.82g, 5.0 mmoles)

was allowed to decompose in benzene (7.8g, 0.1 mmoles) containing 9,10-dimethoxyanthracene (2.38g, 10.0 mmoles) at 50° for 12 hr. The solvent was distilled and replaced with chlorobenzene. Maleic anhydride (2.4g) was added and the mixture heated under reflux for 12 hr. Chromatography on alumina (100g) eluting with petrol gave: biphenyl (0.14g, 7.5 m/100m), m.p. and mixed m.p. after recrystallisation from methanol 68-9°. Eluting with benzene/petrol (1:9) gave, after recrystallisation from petrol (b.p. 60-80°), 9,10-dimethoxytriptycene (0.24g, 15.0 m/100m), m.p. and mixed m.p. 191-2°. (Found : C, 84.31; H, 6.02. $C_{22}H_{18}O_2$ requires C, 84.10; H, 5.74%). M^+ = 314. I.r. and n.m.r. spectra were indistinguishable from those of the authentic sample. Elution with benzene afforded a yellow oil which was recrystallised from chloroform to give long golden needles, m.p. 258-9°. M^+ = 208. (Found : C, 81.07; H, 3.98%). Anthraquinone m.p. 258°, $C_{14}H_8O_2$ requires C, 80.8; H, 3.85%). The i.r. spectrum of the unknown was identical to that of anthraquinone.

11. Reaction with 9-bromoanthracene

N-Nitrosoacetanilide (5.0g, 30.5 mmoles) was allowed to decompose in benzene (78.0g, 1 mole) containing 9-bromoanthracene (9.5g, 30.8 mmoles) at 30° for 24 hr. G.l.c. examination of the reaction

mixture (5% SE-30/190°) showed many products, one of which corresponded to 9-bromotriptycene. After removal of the solvent, the residue was heated under reflux in chlorobenzene (50 ml) containing maleic anhydride (9.5g). This, however, proved ineffective in removing excess 9-bromoanthracene so the mixture was heated for a further 4 days. Chromatography on alumina (300g) eluting with benzene/petrol (1:9) gave a white solid which was recrystallised from petrol (b.p. 60-80°) to give 9-bromotriptycene (0.40g, 4.0 m/100m), m.p. and mixed m.p. 252-4°. M^+ = 332 and 334. The i.r. and n.m.r. spectra were indistinguishable from those of the authentic.

12. Reaction with 9-nitroanthracene

N-Nitrosoacetanilide (6.56g, 40.0 mmoles) was allowed to decompose in benzene (78.0g, 1 mole) containing 9-nitroanthracene (8.92g, 40.0 mmoles) at 50° for 24 hr. G.l.c. examination of the reaction mixture showed many products (5% SE-30/190°), one of which corresponded to 9-nitrotriptycene. The solvent was evaporated and the residue heated under reflux in chlorobenzene (50 ml) containing maleic anhydride (8.9g). This, however as before, proved ineffective in removing excess 9-nitroanthracene so the mixture

was heated for a further 4 days. Chromatography on alumina (300g) eluting with petrol gave biphenyl (0.11g, 2.0 m/100m), m.p. and mixed m.p. after recrystallisation fr m methanol 68-9°. Elution with benzene/petrol (1:1) gave, after recrystallisation from petrol (b.p. 60-80°), 9-nitrotriptycene, (0.08g, 7.0 m/100m), m.p. and mixed m.p. 248°. The i.r. and n.m.r. spectra were indistinguishable from those of the authentic compound.

13. Reaction with 2,3,4,5-tetraphenylcyclopentadiencne in the presence of durene

N-Nitrosoacetanilide (0.41g, 2.5 mmoles) was allowed to decompose in benzene (4.80g, 62.0 mmoles) containing 2,3,4,5-tetraphenylcyclopentadienone (5.25g, 15 mmoles) and durene (2.01g, 15.0 mmoles) at room temperature for 24 hr then heated to reflux temperature. Steam distillation gave a quantitative recovery of durene and chromatography of the residue, after removal of the solvent, on alumina gave, on eluting with benzene/petrol (1:9), after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.48g, 34.0 m/100m), m.p. and mixed m.p. 199-200°. The i.r. spectrum was indistinguishable from that of the authentic. G.l.c. (10% PEGA/175°) indicated that biphenyl was absent. (0.1 m/100m would have been detected).

14. Reaction with 2,3,4,5-tetraphenylcyclopentadienone in the presence of hexamethylbenzene

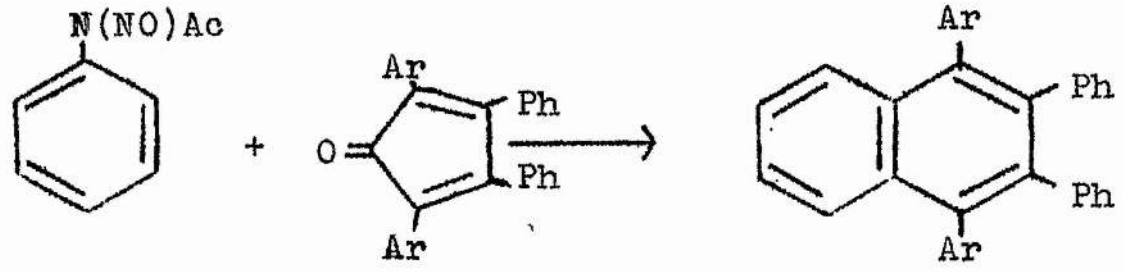
The nitrosamide (0.41g, 2.5 mmoles) was allowed to decompose in benzene containing 2,3,4,5-tetraphenylcyclopentadienone (5.25g, 15.0 mmoles) and hexamethylbenzene (2.4g, 15.0 mmoles) at room temperature for 24 hr then heated to reflux temperature. Chromatography on alumina eluting with petrol gave a quantitative recovery of hexamethylbenzene and eluting with benzene/petrol (1:9) gave, after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.48g, 33.0 m/100m), m.p. and mixed m.p. 199-200°. The i.r. spectrum was indistinguishable from that of the authentic compound. G.l.c. as above indicated the absence of biphenyl.

15. Reaction with 2,3,4,5-tetraphenylcyclopentadienone in acetic acid

The nitrosamide (2.50g, 15.3 mmoles) was allowed to decompose in acetic acid (35.0g, 0.58 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (11.7g, 30.6 m moles) at 50° for 4 days. Chromatography on alumina gave, on eluting with benzene/petrol (1:9), after recrystallisation from acetic acid, 1,2,3,4-tetraphenylnaphthalene (0.26g, 4.0 m/100m), m.p. and mixed m.p.199-200°. I.r. spectrum was identical to that of the authentic.

TABLE 11

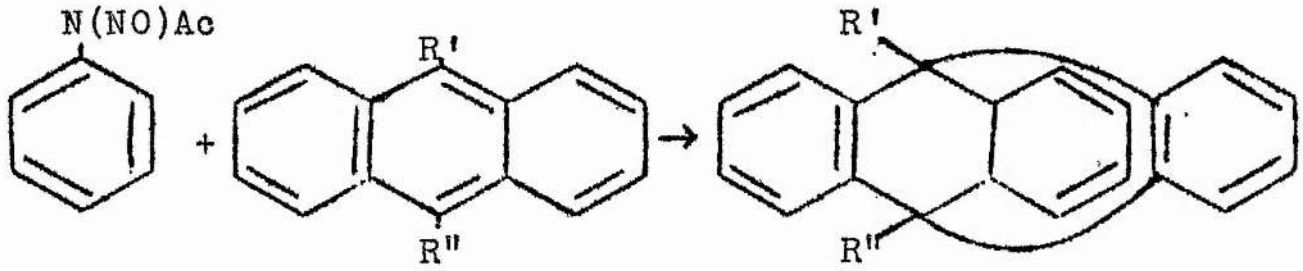
Yields of 1,2,3,4-tetraarylnaphthalenes from the reactions of N-nitrosoacetanilide with 2,3,4,5-tetraarylcyclopentadienones



Ar	Solvent	Yield (m/100m)
Ph	Benzene	22.0
Ph	Furan	1.4
Ph	Benzene/durene	34.0
Ph	Benzene/hexamethylbenzene	33.0
Ph	Acetic acid	4.0
p-Me-C_6H_4	Benzene	82.0
p-OMe-C_6H_4	Benzene	82.0
p-$MeSO_2$-C_6H_4	Carbon tetrachloride	19.0

TABLE 12

Yields of triptycenes from the reactions of N-nitroso-acetanilide with anthracenes



R'	R''	Solvent	Yield (m/100m)
H	H	Benzene	5.0
CH_3	CH_3	Benzene	30.0
OCH_3	OCH_3	Benzene	15.0
Br	H	Benzene	4.0
NO_2	H	Benzene	7.0

B Reactions of o-t-butyl-N-nitrosoacetanilide

1. Reaction with anthracene

o-t-Butyl-N-nitrosoacetanilide (2.80g, 13.0 mmoles) was allowed to decompose in benzene (40.0g, 0.52 moles) containing anthracene (4.62g, 26.0 mmoles) at room temperature for 16 hr. The reaction mixture was then heated slowly to reflux to complete the reaction. The benzene was distilled and replaced with

chlorobenzene; maleic anhydride (4.6g) was added and the mixture heated under reflux for 12 hr. The chlorobenzene was distilled off and the residue chromatographed on alumina (300g). Elution with benzene/petrol (1:9) gave a white fluorescent solid, which after recrystallisation from petrol (b.p. 60-80°) gave, 1-t-butyltriptycene (0.76g, 19.3 m/100m), m.p.209°. M^+ = 310.

N.m.r. ($CDCl_3$) : τ 2.80 (centre of aromatic pattern), 3.80 (bridgehead H_9), 4.60 (bridgehead H_{10}) and 8.50 (s, t-butyl).

(Found : C, 92.70; H, 7.05. $C_{24}H_{22}$ requires C, 92.91; H, 7.09%).

Using the isolated yield of adduct as an internal standard, g.l.c. analysis (2% NPGS/225°) of the reaction mixture, using the Pye 104 instrument, gave: o-t-butylphenyl acetate (23.0 m/100m), and m-t-butylphenyl acetate (< 0.1).

Elution with petrol/benzene (4:1) gave a red-black solid (0.20g) and with benzene, a black tar (0.60g).

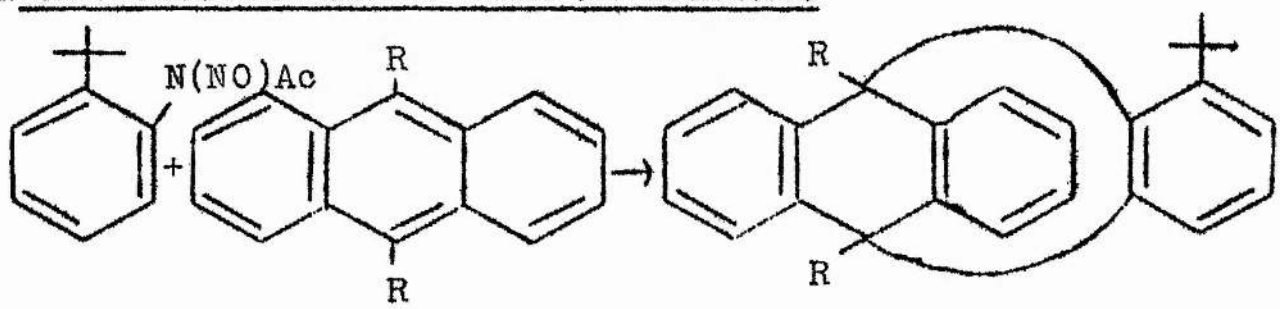
2. Reaction with 9,10-dimethoxyanthracene

o-t-Butyl-N-nitrosoacetanilide (1.0g, 4.5 mmoles) was allowed to decompose in benzene (20.0g, 0.26 moles) containing 9,10-dimethoxyanthracene (2.16g,

9.0 mmoles) at room temperature for 16 hr then heated slowly to reflux to complete the reaction. Benzene was distilled off and replaced with chlorobenzene. Maleic anhydride (2.16g) was added and the mixture heated under reflux for 12 hr. Chlorobenzene was distilled off and the residue chromatographed on alumina (100g). Elution with petrol/benzene (9:1) gave, after recrystallisation from petrol (b.p. 60-80°), 1-t-butyl-9,10-dimethoxytriptycene (0.07g, 4.2 m/100m). M^+ = 370. M.p. 235.5-236°.
(Found : C, 84.60; H, 7.11. $C_{26}H_{26}O_2$ requires C, 84.30; H, 7.03%).
N.m.r. ($CDCl_3$) : τ 2.30-3.30 (complex, 11 H), 5.70 and 5.93 (OCH_3, 6 H) and 8.43 (s, t-butyl).
Using the isolated yield of adduct as an internal standard, g.l.c. analysis (2% NPGS/225°) gave: o-t-butylphenyl acetate (15.0 m/100m), and m-t-butylphenyl acetate (< 0.1).
Elution with petrol/benzene (4:1) gave a red oil (1.18g) and with benzene, a black tar (0.50g).

TABLE 13

Yields of triptycenes from the reactions of o-t-butyl-N-nitrosoacetanilide with anthracenes



R	Solvent	Yield (m/100m)
OCH_3	Benzene	4.2
H	Benzene	19.3

XV COMPETITION REACTIONS

A General technique

Competition reactions involved the reaction of an aryne source with an excess of an equimolar mixture of two arynophiles which was either (a) a mixture of 2,3,4,5-tetraarylcyclopentadienones or (b) a mixture of anthracenes. After reaction, the mixture was treated with maleic anhydride in chlorobenzene, and after removal of the solvent, the residue was chromatographed on alumina, and the molar ratio, K_2^1 where K_2^1 = moles of adduct 1/moles of adduct 2, computed in (a) by measuring the individual areas of

the two methyl absorptions in the n.m.r. spectrum of the mixture (CH_3 = 7.72 τ, OCH_3 = 6.26 τ, and SO_2CH_3 = 7.00 τ). A Varian HA-100 n.m.r. spectrometer was used, and the integral values taken as the mean of at least three readings. The quantitative response of the instrument was confirmed with known mixtures of adducts. The error involved in the measurement of the n.m.r. integral was $\pm$ 2 mm on each reading, thus giving a total error in the quotient of $\pm$ 8 mm. This amounted at maximum to an error of $\pm$ 10%.

To check for random error, control experiments were performed which showed that mixtures of adducts, when subjected to the complete workup procedure, were recovered quantitatively, and the difference involved in the n.m.r. measurement of K_2^1 before and after workup was always within the $\pm$ 10% calculated error.

In (b), the ratio K_2^1 was measured by g.l.c. (Pye 104 and Varian Aerograph 1520B) and as above the instrument calibrated with known mixtures of adducts. Area measurements of g.l.c. peaks showed, at maximum, a variance of $\pm$ 5%, the total error in the quotient is thus $\pm$ 10%. Again random error was checked for by control experiments which showed that the difference in K_2^1 before and after workup was

always within the ± 10% calculated error.

B Reactions of N-nitrosoacetanilide

1. Reaction with 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone and 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone

N-Nitrosoacetanilide (0.16g, 1.0 mmole) was allowed to decompose in benzene (39.0g, 0.5 moles) containing 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (2.29g, 5.1 mmoles) and 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone (2.12g, 5.1 mmoles) at 20° for 12 hr then heated for 2 hr under reflux. The excess arynophiles were removed by heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (5.0g) for 12 hr and after evaporation of the chlorobenzene, the residue was chromatographed on alumina (200g). Elution with much benzene ensured that all the aryne adducts were collected. Quantitative n.m.r. ($CDCl_3$) of the residue gave the value of $K_{Me}^{OMe} = 1.0$.

A parallel reaction using carbon tetrachloride as solvent instead of benzene gave $K_{Me}^{OMe} = 1.0$.

2. Reaction with 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone and 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone

N-Nitrosoacetanilide (0.082g, 0.5 mmoles) was

allowed to decompose in carbon tetrachloride (40.0g, 0.26 moles) containing 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (0.51g, 1.2 mmoles) and 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone (0.49g, 0.9 mmoles) at 20° for 12 hr then heated under reflux for 2 hr. Workup and chromatography as described above gave, on eluting with much chloroform a mixture of the two aryne adducts. Quantitative n.m.r. ($CDCl_3$) gave the value of the competition constant as $K^{OMe}_{SO_2Me} = 2.2$

3. Reaction with 1,4-dimethoxyanthracene in benzene

N-Nitrosoacetanilide (0.82g, 5.0 mmoles) was allowed to decompose in benzene (7.8g, 0.1 mole) containing 1,4-dimethoxyanthracene (2.38g, 10.0 mmoles) at 50° for 12 hr. Analysis of the reaction mixture by g.l.c. (5% SE-30/180°; 2% APL/200°) using the authentic samples of A-ring and B-ring adducts provided by Dr B.H.Klanderman for peak enhancement, identified 1,4-dimethoxytriptycene and 5,12-dimethoxy-5,12-dihydro-5,12-ethenonaphthacene. Quantitative measurements gave the value of the competition constant as $K^{B}_{A} = 2.6$.

4. Reaction with 9,10-dimethoxyanthracene and anthracene

N-Nitrosoacetanilide (0.41g, 2.5 mmoles) was

allowed to decompose in benzene (39.0g, 0.5 moles) containing anthracene (1.78g, 10.0 mmoles) and 9,10-dimethoxyanthracene (2.38g, 10.0 mmoles) at 50° for 12 hr. Excess anthracene and 9,10-dimethoxyanthracene were removed by heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (4.0g). Chromatography on alumina (100g) eluting with much benzene, gave a mixture of the two triptycenes. Analysis by g.l.c. (5% SE-30/200°; 2% NPGS/200°) gave the value of the competition constant as K_H^{OMe}=3.2.

5. Reaction with 9,10-dimethylanthracene and anthracene

N-Nitrosoacetanilide (0.41g, 2.5 mmoles) was allowed to decompose in benzene (39.0g, 0.5 moles) containing 9,10-dimethylanthracene (2.06g, 10.0 mmoles) and anthracene (1.78g, 10.0 mmoles) at 50° for 12 hr. Excess anthracene and 9,10-dimethylanthracene were removed by heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (4.0g) and chromatography on alumina (100g) eluting with much benzene gave the mixture of triptycenes. Analysis by g.l.c. (5% SE-30/200°; 2% NPGS/200°) gave the value of the competition constant as K_H^{Me} = 19.7.

6 Reaction of o-t-butyl-N-nitrosoacetanilide with 9,10-dimethoxyanthracene and anthracene

o-t-Butyl-N-nitrosoacetanilide (0.55g, 2.5 mmoles)

was allowed to decompose in benzene (20.0g, 0.26 moles) containing anthracene (1.78g, 10.0 mmoles) and 9,10-dimethoxyanthracene (2.38g, 10.0 mmoles) at room temperature for 16 hr. The mixture was then heated slowly to reflux. The benzene was replaced with chlorobenzene (25 ml), maleic anhydride (4.1g) was added and the mixture heated under reflux for 12 hr. The chlorobenzene was distilled off and the residue chromatographed on alumina (100g). Elution with much benzene ensured that all the triptycenes were collected. G.l.c. analysis (5% SE-30/200°; 2% NPGS/225°) gave the value of the competition constant as $K^{H}_{OMe} = 13.5$.

D Competition reactions using pentyl nitrite and anthranilic acid

1. Reaction with 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone and 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone

Anthranilic acid (0.027g, 0.2 mmoles) in benzene (1 ml) was added to a solution of pentyl nitrite (0.03g, 0.25 mmoles) in benzene (25.0g, 0.32 moles) containing 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (0.61g, 1.37 mmoles) and 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone (0.60g, 1.45 mmoles) at 50° and the solution stirred for 4 hr. The solvent

was evaporated and replaced with chlorobenzene (25 ml); maleic anhydride (1.5g) was added and the mixture heated under reflux for 12 hr. Chromatography on alumina (100g) eluting with much benzene gave the mixture of adducts. Quantitative n.m.r. ($CDCl_3$) gave the value of the competition constant as $K_{Me}^{OMe} = 1.0$.

A parallel experiment with carbon tetrachloride as solvent instead of benzene gave $K_{Me}^{OMe} = 1.0$.

2. Reaction with 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone and 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone

Anthranilic acid (0.027g, 0.2 mmoles) in carbon tetrachloride (1 ml) was added to a solution of pentyl nitrite (0.03g, 0.25 mmoles) in carbon tetrachloride containing 2,5-di-p-methylsulphonylphenyl-3,4-diphenylcyclopentadienone (0.46g, 0.8 mmoles) and 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (0.46g, 1.0 mmoles) at 50°, and the solution stirred for 4 hr. After removal of the solvent, and heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (1.0g), chromatography on alumina (100g) eluting with much chloroform gave the mixture of adducts. Quantitative n.m.r. ($CDCl_3$) gave the value of the competition constant as $K_{SO_2Me}^{OMe} = 2.1$.

3. Reaction with 1,4-dimethoxyanthracene

Anthranilic acid (0.03g, 0.22 mmoles) in benzene (1 ml) was added to a solution of pentyl nitrite (0.03g, 0.25 mmoles) in benzene (10.0g 0.13 moles) containing 1,4-dimethoxyanthracene (0.50g, 2.1 mmoles) at 50° and the solution stirred for 4 hr. G.l.c. analysis of the reaction mixture (5% SE-30/ 180°; 2% APL/200°) gave the value of the competition constant as $K_A^B = 2.6$.

4. Reaction with 9,10-dimethoxyanthracene and anthracene

Anthranilic acid (0.37g, 2.7 mmoles) in benzene (1 ml) was added slowly to a solution of pentyl nitrite (0.37g, 3.1 mmoles) in benzene (20.0g, 0.26 moles) containing 9,10-dimethoxyanthracene (2.38g, 10.0 mmoles) and anthracene (1.78g, 10.0 mmoles) at 50° and the solution stirred for 4 hr. After removal of the solvent and heating under reflux with maleic anhydride (4.0g) in chlorobenzene (25 ml); chromatography on alumina, eluting with much benzene gave the mixture of adducts. Analysis by g.l.c (5% SE-30/200°; 2% NPGS/ 200°) gave the value of the competition constant as $K_H^{OMe} = 3.1$.

5. Reaction with 9,10-dimethylanthracene and anthracene

Anthranilic acid (0.02g, 0.13 mmoles) in benzene (1 ml) was added slowly to a solution of pentyl nitrite (0.02g, 0.17 mmoles) in benzene (20.0g, 0.26 mmoles) containing anthracene (0.11g, 0.60 mmoles) and 9,10-dimethylanthracene (0.12g,0.58 mmoles) at 50° and the solution stirred for 4 hr. After removal of the solvent and heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (0.5g), chromatography on alumina gave, on eluting with much benzene, the mixture of adducts. G.l.c. analysis (5%SE-30/200°; 2% NPGS/200°) gave the value of the competition constant as $K_H^{Me} = 19.5$.

E Reaction of 1-aminobenzotriazole and lead tetra-acetate with 2,5-di-p-methoxyphenyl-3,4-diphenyl-cyclopentadienone and 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone

Lead tetraacetate (0.18g) was added to a solution containing 1-aminobenzotriazole (0.03g, 0.22 mmoles), 2,5-di-p-methoxyphenyl-3,4-diphenylcyclopentadienone (0.45g, 1.0 mmoles) and 2,5-di-p-methylphenyl-3,4-diphenylcyclopentadienone (0.45g, 1.1 mmoles) in benzene (39.0g, 0.5 moles) at 20° and the mixture stirred for 4 hr. After evaporation of the solvent

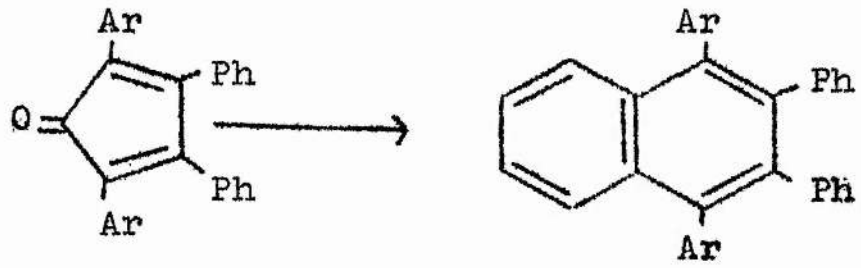
and heating under reflux in chlorobenzene (25 ml) containing maleic anhydride (1.5g) for 12 hr; chromatography on alumina (100g) eluting with much benzene afforded the mixture of adducts. N.m.r. ($CDCl_3$) gave the value of the competition constant as K^{OMe}_{Me} = 1.0.

F Reaction of potassium t-butoxide and o-t-butylbromobenzene with 9,10-dimethoxyanthracene and anthracene

A mixture of potassium t-butoxide (0.28g, 2.5 mmoles), o-t-butylbromobenzene (0.56g, 5.0 mmoles), anthracene (1.78g, 10.0 mmoles) and 9,10-dimethoxyanthracene (2.38g, 10.0 mmoles) in t-butylbenzene (50 ml) was heated under reflux for 18 hr. Maleic anhydride (5.0g) was added and the mixture heated under reflux for a further 12 hr. After removal of the solvent, chromatography on alumina (100g) eluting with much benzene ensured that all the adducts were collected. G.l.c. analysis (5% SE-30/200°; 2% NPGS/225°) gave the value of the competition constant as K^{H}_{OMe} = 13.3.

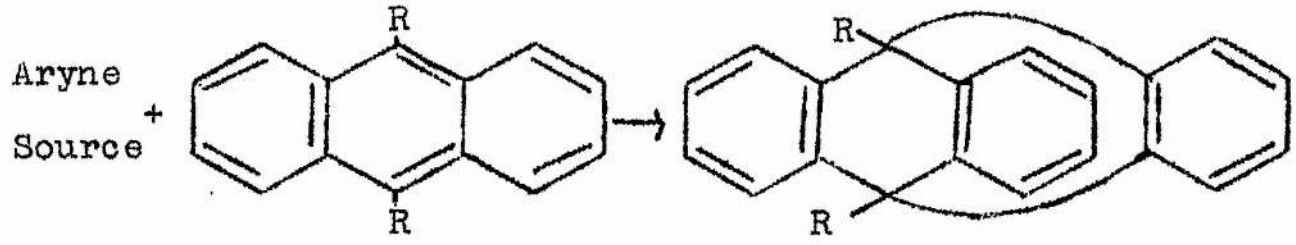
TABLE 14

Competition Reactions

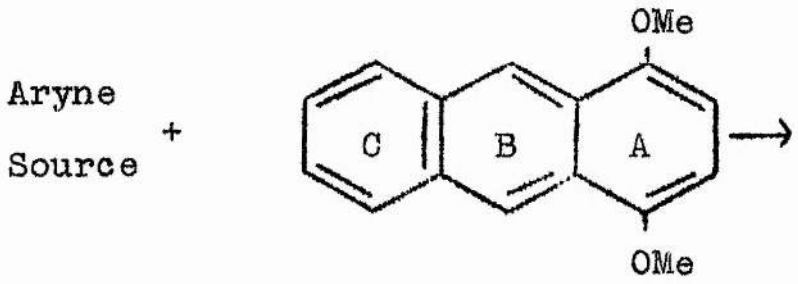
Aryne Source + 

Arynophile pairs	Solvent	Competition constant NNA	PN/AA	AB
Ar = p-MeC_6H_4, p-$MeOC_6H_4$	Benzene	K_{Me}^{OMe} = 1.0 ,	1.0 ,	1.0
p-MeC_6H_4 p-$MeOC_6H_4$	CCl_4	K_{Me}^{OMe} = 1.0 ,	1.0	
p-$MeSO_2C_6H_4$ p-$MeOC_6H_4$	CCl_4	$K_{SO_2Me}^{OMe}$ = 2.2 ,	2.1	

Abbreviations used represent N-nitrosoacetanilide (NNA), pentyl nitrite/anthranilic acid (PN/AA) and 1-amino-benzotriazole/lead tetraacetate (AB).



Arynophile pairs	Solvent	Competition constant N.N.A.	P.N./A.A.
R = OCH_3, H	PhH	K_H^{OMe} = 3.2	3.1
CH_3, H	PhH	K_H^{Me} = 19.7	19.5



A-ring adduct

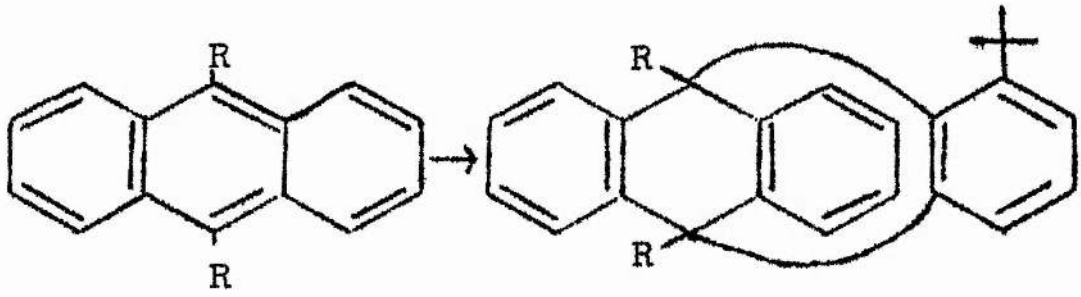
B-ring adduct

Arynophile pair	Solvent	Competition constant N.N.A.	P.N./A.A.
A-ring, B-ring	Benzene	K_A^B = 2.6	2.6

For formulation of the A-ring and B-ring adducts see Introduction, page 34.

TABLE 15

Competition reactions of o-t-Butyl-N-nitrosoacetanilide

Aryne Source + 

Arynophile pair	Solvent	Competition constant	
		o-Bu^{t}NNA	ArBr/KOBu^t
R = OCH_3, H	Benzene	K^H_{OMe} = 13.5 ,	13.3

Abbreviations used represent o-t-butyl-N-nitrosoacetanilide (o-Bu^{t}NNA) and o-t-butylbromobenzene (ArBr).

XVI OTHER REACTIONS OF ACYLARYLNITROSAMINES

A Reactions of N-nitroso-N-acylanthranilic acids

1. Reaction of N-nitroso-N-formylanthranilic acid with 2,3,4,5-tetraphenylcyclopentadienone

N-Nitroso-N-formylanthranilic acid (0.74g, 3.8 mmoles) was allowed to decompose in benzene (29.0g, 0.37 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (2.5g, 6.5 mmoles) at 18° for 2 hr. The solution was then heated under reflux for a further 2 hr.

Analysis of a small portion of the solution by g.l.c. (2% NPGS/100°) using biphenyl as marker gave: 3,1-benzoxazin-4-one (16.8 m/100m). Chromatography of the bulk of the solution on alumina (100g) gave, on eluting with benzene/petrol (1:9) a white solid (0.35g) which was recrystallised from acetic acid to give 1,2,3,4-tetraphenylnaphthalene (0.24g, 15.0 m/100m); m.p. and mixed m.p. 199-200°. The i.r. spectrum was indistinguishable from that of the authentic.

A parallel reaction allowed the 3,1-benzoxazin -4-one to be separated by distillation, b.p. 110-20°/0.4 mm, m.p. 40-50°. The n.m.r. and i.r. spectra were identical to those of the authentic. Elemental analysis was not performed because of the ease with which the product decomposed.

2. Reaction of (impure) N-nitroso-N-acetylanthranilic acid with 2,3,4,5-tetraphenylcyclopentadienone

N-Nitroso-N-acetylanthranilic acid (2.97g, 14.3 mmoles), containing some N-acetylanthranilic acid formed by denitrosation, was allowed to decompose in benzene (26.79g, 0.34 moles) containing 2,3,4,5-tetraphenylcyclopentadienone (8.61g, 22.4 mmoles) at 15° for 12 hr, then heated under reflux for 6 hr. Chromatography on alumina (1000g) gave, on eluting

with benzene/petrol (1:9) a white solid, which was recrystallised from acetic acid to give 1,2,3,4-tetraphenylnaphthalene (0.37g, 6.0 m/100m); m.p. and mixed m.p. 199-200°. The i.r. spectrum was indistinguishable from that of the authentic compound. G.l.c. analysis (2% NPGS/120°) using biphenyl as marker gave: 2-methyl-3,1-benzoxazin-4-one (16.0 m/100m).

A parallel experiment allowed this compound to be separated by distillation, b.p. 89/0.4 mm, m.p. 76-7°. After recrystallisation from a mixture of ethyl acetate/hexane (1:1) the m.p. and mixed m.p. were 80-1°. The n.m.r. and i.r. spectra were identical to those of the authentic.

A control experiment heating N-acetyl and N-formyl-anthranilic acid with benzene for 12 hr under reflux showed no 2-methyl-3,1 benzoxazin-4-one or 3,1-benzoxazin-4-one respectively; g.l.c. (2% NPGS/120° and 100°).

B N-Nitrosoacetanilide

1. Reaction with diethyl maleate in benzene

N-Nitrosoacetanilide (10.0g, 0.06 moles) was allowed to decompose in benzene (18.0g, 0.23 moles) containing diethyl maleate (21.0g, 0.16 moles) at

room temperature for 48 hr then heated under reflux for 2 hr. G.l.c. (2% NPGS/80-130°) showed only biphenyl. Distillation of the reaction mixture gave a quantitative recovery of diethyl maleate.

2. Reaction with acrylonitrile

N-Nitrosoacetanilide (8.5g, 0.05 moles) was allowed to decompose in benzene (85.4g, 1.1 moles) containing acrylonitrile (6.46g, 0.12 moles) at room temperature. After an induction period, a vigorous reaction set in, and much polymeric material was rapidly formed. G.l.c. (2% NPGS/60-150°) showed no products and n.m.r. showed only aromatic protons.

3. Reaction with tetracyanoethylene

N-Nitrosoacetanilide (1.64g, 10.0 mmoles) was allowed to decompose in benzene (15.6g, 0.2 mmoles) containing tetracyanoethylene (3.84g, 20.0 mmoles) at room temperature for 24 hr. G.l.c. examination (2% NPGS/ 175°) showed biphenyl as the only product.

4. Reaction with dimethylacetylenedicarboxylate

N-Nitrosoacetanilide (14.0g, 85.0 mmoles) was allowed to decompose in benzene (137g, 1.76 moles) containing dimethylacetylenedicarboxylate (37.0g, 0.26 moles) at room temperature. After a short induction period, a vigorous reaction set in and the reaction

was quickly over. After removal of the benzene, and distillation of the excess dimethylacetylenedicaboxylate, the residue was distilled from a Woods-metal bath to give the following fractions: (a) yellow, low-melting solid (1.0g), b.p.90-120°/0.5 mm, (b) yellow-red oil (3.90g), b.p. 170-200°/0.5 mm, (c) red oil (4.50g), b.p. 200-250°/0.5 mm.

Fraction (a) was recrystallised from methanol to give biphenyl (0.90g, 7.0 m/100m), m.p. and mixed m.p. 68-9°. The i.r. spectrum was identical to that of the authentic.

Fraction (b) was recrystallised from methanol to give cream-coloured crystals (3.60g) m.p. 80-100°. G.l.c. (2% NPGS/175°) showed it to be a mixture (2:1) of two compounds. Fractional crystallisation from methanol afforded a pure sample of the minor component, m.p. 141-141.5°.

(Found; C, 73.23; H, 5.37. $C_{18}H_{16}O_4$ requires C, 73.0; H, 5.41%). M^+ = 296.

I.r. (Nujol): 1725 cm^{-1} (C=O).

N.m.r. ($CDCl_3$) : τ 2.64 (s, 10H) and 6.50 (s, 6H).

Unknown is <u>trans</u>-dimethyl diphenylmaleate.

A sample of the major product was separated by preparative g.l.c. using the D.6 instrument (2% NPGS/

175°) to give a white crystalline solid, m.p.108-110°, cis-dimethyl diphenylmaleate (lit.,[156] 110-2°).

I.r. (Nujol): 1725 cm^{-1}(C=O). M^+ = 296.

N.m.r. ($CDCl_3$): τ 2.60-3.10 (complex, 10H) and 6.20 (s, 6H).

A sample of the mixture was hydrogenated with 10% palladium on carbon powder catalyst in ethanol to give a mixture of meso and dl-dimethyl diphenylsuccinate.

(Found: C, 72.73; H, 6.08. $C_{18}H_{18}O_4$ requires C, 72.52; H, 6.03%). M^+ = 298.

I.r. (Nujol): 1725 cm^{-1}. The i.r. spectrum was indistinguishable from that of an authentic sample of meso-dimethyl diphenylsuccinate provided by Dr.J.T. Sharp.

N.m.r. ($CDCl_3$): τ 2.30-2.80 (complex, 10H), 5.60 (s, 2H) and 6.60 (s, 6H) The n.m.r. spectrum was also indistinguishable from that of meso-dimethyl diphenyl succinate. Overall yields by g.l.c. of the diesters were : trans-dimethyl diphenylmaleate (5.0 m/100m and cis-dimethyl diphenylmaleate (10.0).

Fraction (c) was recrystallised from methanol to give long needles of 1,2,3,4-tetracarbomethoxynaphthalene, m.p. 145-6°. M^+ = 360.

(Found: C, 60.02; H, 4.44. $C_{18}H_{16}O_8$ requires C,59.9; H, 4.45%).

I.r. (Nujol): 1725 cm^{-1} (C=O).

N.m.r. ($CDCl_3$): τ 1.85-2.05 and 2.25-2.45 (two symmetrical quartets, A_2B_2, 4H), 6.00 (s, 6H) and 6.11 (s, 6H).

No change in the n.m.r. spectrum was observed after a portion of the material was subjected to hydrogenation as above with 10% palladium on carbon powder catalyst in ethanol.

A small portion of this solid was heated under reflux with activated copper powder and quinoline for 3 hr. G.l.c. analysis (3% APL/140°; 2% NPGS/100°) confirmed the presence of naphthalene.

A control experiment showed that heating phenylazotriphenylmethane in benzene containing dimethylacetylenedicarboxylate gave biphenyl and triphenylmethane as the only products.

5. Reaction with deuteroacetic acid

N-Nitrosoacetanilide (1.34g, 8.2 mmoles) was allowed to decompose in deuteroacetic acid (15.0g, 0.25 moles) at 50° for 4 days. Excess deuteroacetic acid was removed and phenyl acetate b.p. 195° was distilled out (ca. 50 m/100m). Mass spectral analysis

showed no M^+ due to o-deuterophenyl acetate (M^+ = 137). Less than 1% would have been detected in the product which had a mass spectrum indistinguishable from that of phenyl acetate as was the i.r. spectrum.

C p-t-Butyl-N-nitrosoacetanilide

p-t-Butyl-N-nitrosoacetanilide (11.0g, 50 mmoles) was allowed to decompose in benzene (156g) containing dimethylacetylenedicarboxylate (28.4g, 0.2 moles) at room temperature for 24 hr. After removal of benzene and dimethylacetylenedicarboxylate, the residue was distilled to give the following fractions: (a) yellow low-melting solid, b.p. 90-100°/0.1 mm, and (b) red-black solid, b.p. 160-220°/0.02 mm. Fraction (a) was recrystallised from methanol to give p-t-butylbiphenyl (2.4g, 25.0 m/100m), m.p. and mixed m.p. 51.5-52°. I.r. spectrum was identical to that of the authentic sample.

Fraction (b) was recrystallised from petrol (b.p. 60-80°) to give p-t-butylacetanilide (0.36g, 4.0 m/100m). The residue left after evaporation of the solvent in the mother liquor was chromatographed on silica. Eluting with benzen/petrol (1:9) gave(a) a yellow oil (0.1g) and (b) a red oil (2.0g). The latter fraction was distilled in a Woods-metal bath, b.p.

190-220°.

(Found: C, 75.8; H, 7.5. $C_{22}H_{24}O_4$ requires C, 75.0, H, 6.82%). This material was unchanged by attempted hydrogenation with palladium on carbon catalyst. Under these conditions, dimethyl 1-phenyl-2-p-t-butylphenylmaleate would have been hydrogenated.

XVII ADDENDA

A Reaction of pentyl nitrite and anthranilic acid with dimethylacetylenedicarboxylate in benzene

Anthranilic acid (5.0g, 0.04 moles) in benzene (20 ml) was added dropwise to a refluxing solution containing pentyl nitrite (5.2g) and dimethylacetylene-dicarboxylate (16.0g, 0.11 moles) in benzene (25g, 0.32 moles). After the addition was complete, the benzene was evaporated and the excess dimethylacetylene-dicarboxylate distilled. The residue was then distilled in a Woods metal bath and one fraction(1.0g, b.p. 200-250°/0.1 mm) only was collected. This brown oil was triturated with methanol, and recrystallised from methanol to give 5,6,11,12-tetracarbomethoxy-dibenzo[a,e]cyclooctatetraene (0.48g, 3.0 m/100m). M.p. 213-5° (decomp.). M^+ = 436.

(Found: C, 65.67; H, 4.58. $C_{24}H_{20}O_8$ requires C, 66.05; H, 4.58%).

I.r. (Nujol): 1720 cm^{-1}(C=O).

N.m.r. ($CDCl_3$): τ 2.81 and 2.83 (d, 8H) and 6.18 (s, 12H).

The crude reaction product was examined by n.m.r. for trace amounts of 1,2,3,4-tetracarbomethoxynaphthalene, but this was absent, as were the cis-, and trans-dimethyl diphenylmaleates.(0.2% Would have been detected).

DISCUSSION

DISCUSSION

At the outset of this investigation, there were two main problems associated with the decomposition of acylarylnitrosamines in solution. First the question of aryne participation, and second, the unexplained formation of diazonium halides in halogenomethanes. Investigations of both problems were therefore initiated.

I The reaction of N-nitrosoacetanilide with benzene

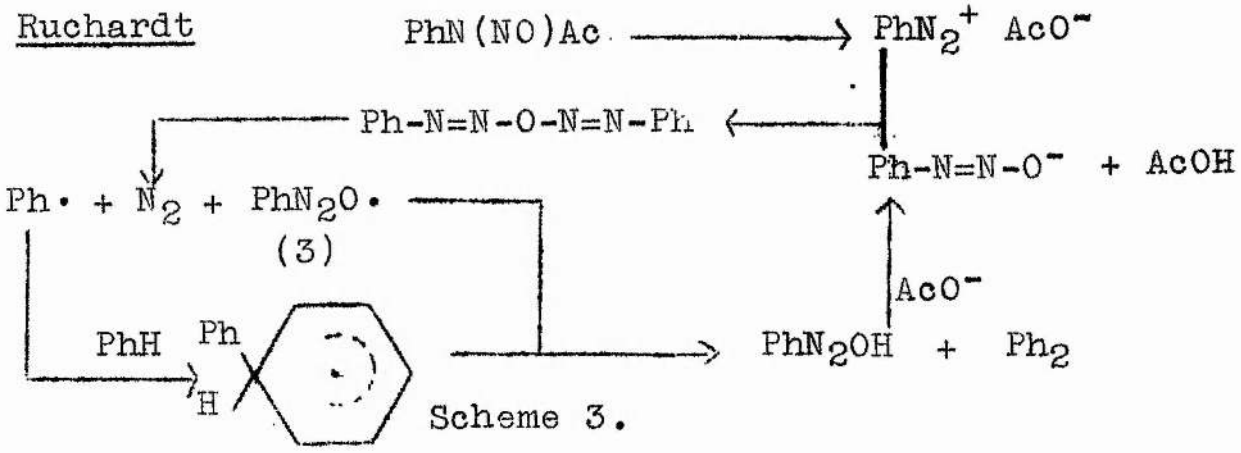
The decomposition of N-nitrosoacetanilide in benzene has been the subject of much attention since the reaction was first studied by Bamberger [45] in 1897, who showed that the products were biphenyl,

$$PhN(NO)Ac \xrightarrow{PhH} Ph_2 + N_2 + AcOH$$

nitrogen and acetic acid.

Recently the reaction mechanism has been rationalised by Ruchardt and Freudenberg [68] in terms of a free radical chain mechanism, with the phenyl diazotate radical (3) as chain carrier (Scheme 3), and these

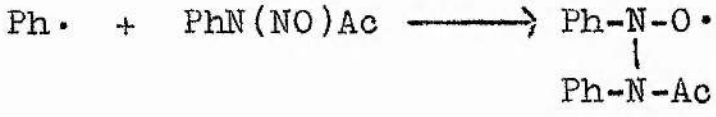
Ruchardt



Scheme 3.

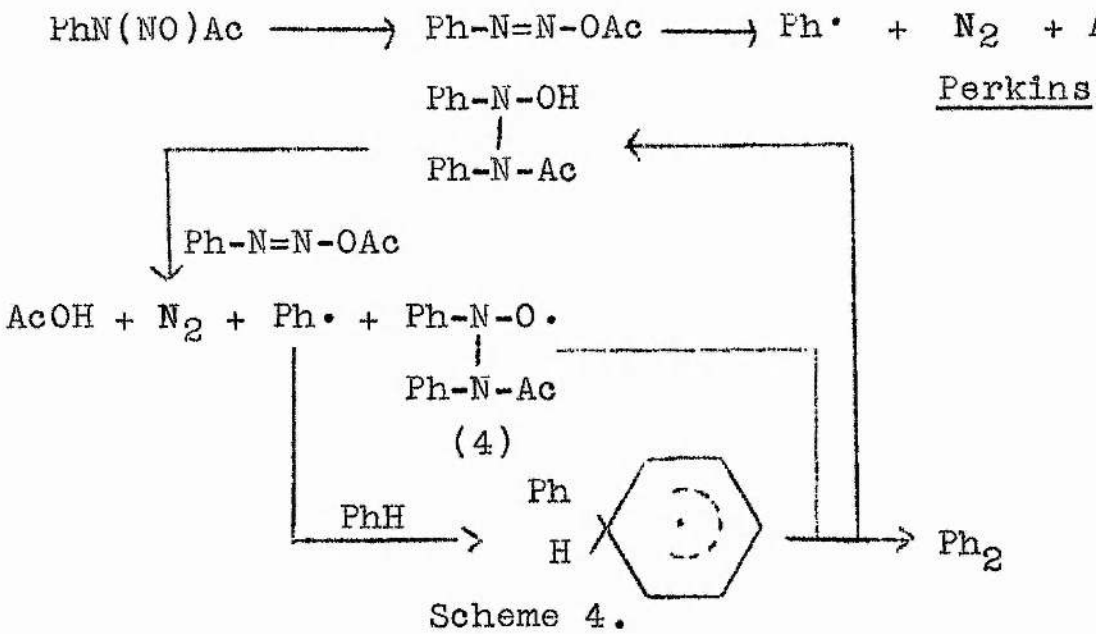
workers supported their claim with the observation of an e.s.r. signal, which they attributed to (3), when the reaction was done in the cavity of an e.s.r. spectrometer.

Later work by Perkins *et al.*[71] showed that the radical observed in the e.s.r. spectrum was in fact that of a nitroxide, (*N*-phenylacetamido) phenyl nitroxide (PAPN) (4), formed by the addition of a



(4)

free phenyl radical to *N*-nitrosoacetanilide, and revised the Ruchardt mechanism accordingly (Scheme 4):



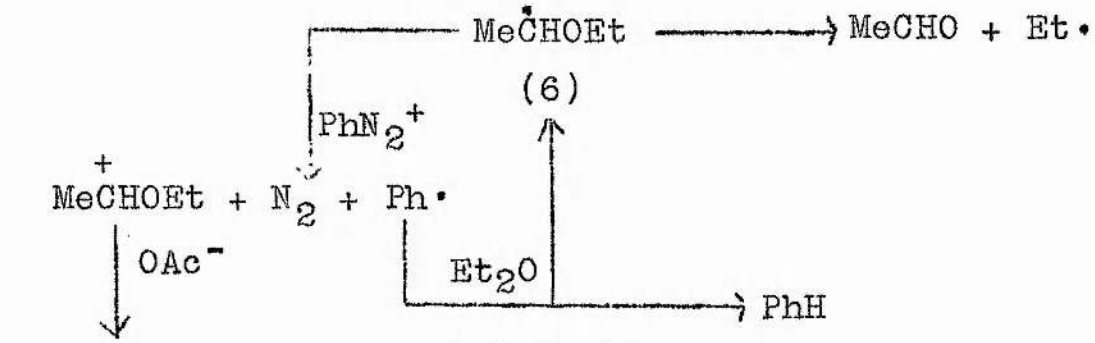
Scheme 4.

The modifications to the Ruchardt scheme, however, do not invalidate its fundamental concepts, and formation

of biphenyl is via an analogous process using the PAPN radical (4) as chain carrier.

Cadogan et al.[74] later showed that in addition to the e.s.r. signal due to the PAPN radical, there was also a weak signal which they attributed to the phenyl diazotate radical (3). This signal was observable in benzene only at high modulation, but was more clearly seen in solvents having an easily abstractable hydrogen, e.g., cumene, in which the signal due to the PAPN radical was absent.

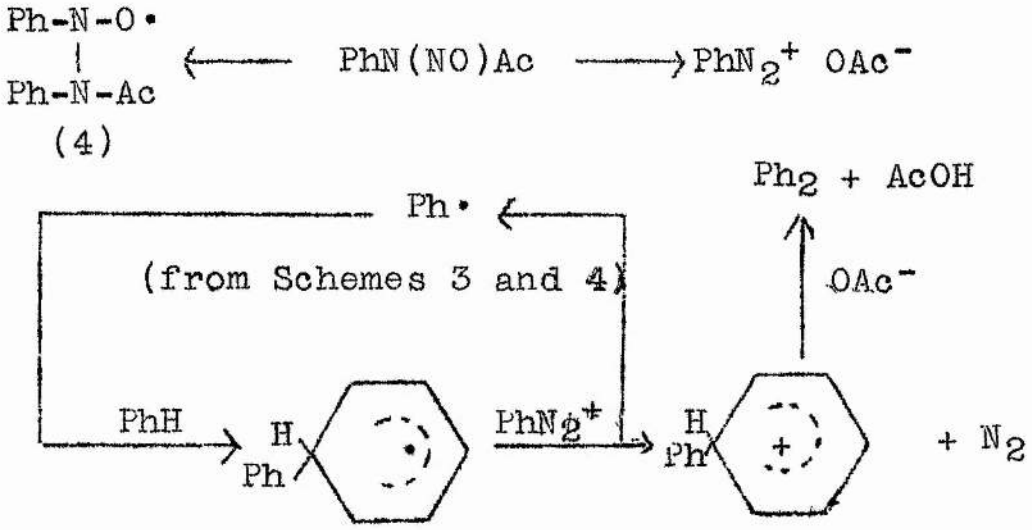
Later work[76] by these researchers on the decomposition of N-nitrosoacetanilide in diethyl ether led them to postulate a redox reaction between the aryldiazonium cation and the intermediate radical (6), leading to the formation of a phenyl radical, which then became the chain carrier (Scheme 5):



Scheme 5.

These workers now believe that a similar redox reaction may be operative in benzene[164], and is a significant contributor to the chain mechanism of decomposition

of acylarylnitrosamines (Scheme 6) and that the



Scheme 6.

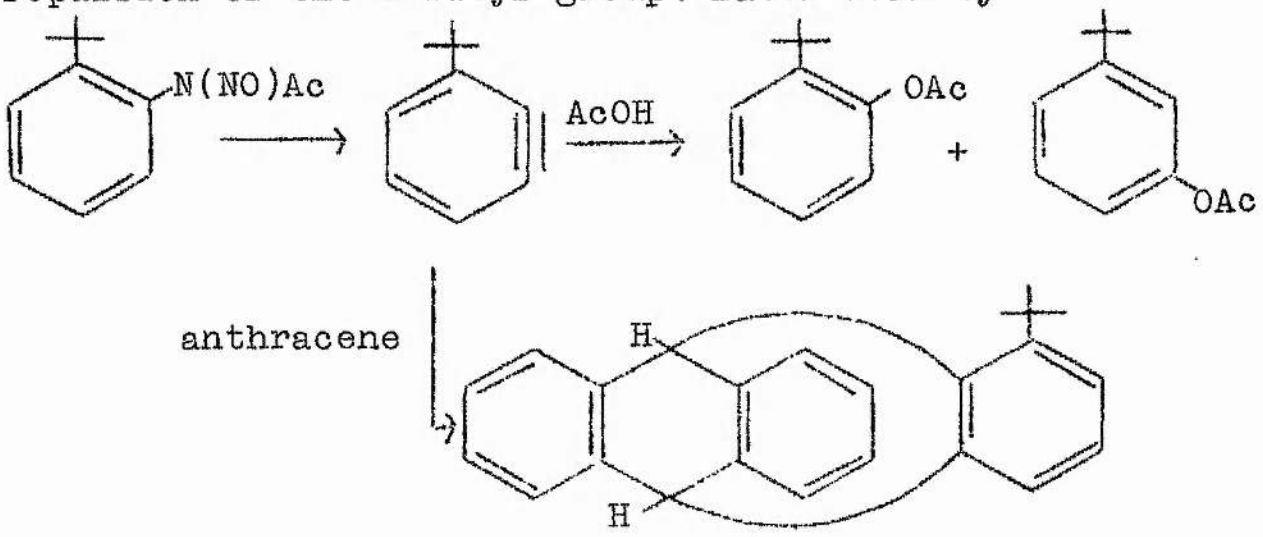
production of the PAPN radical (4) and diazotate radical (Ph-N=N-O•) may be incidental to the main product forming sequence.

II The question of aryne participation

The mechanism of the decomposition of N-nitrosoacetanilide in benzene has been discussed above in terms of current research results. However, of the mechanisms proposed, none account for the surprising formation of aryne adducts in the reactions of acylarylnitrosamines with arynophiles in both benzene and halogenated solvents.

In 1964, Cadogan and Hibbert [79] observed that the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene gave a low yield of 2-t-butylbiphenyl along

with a high yield of the o-, and m-t-butylphenyl acetates. They rationalised this by postulating the intermediacy of 3-t-butylbenzyne, which would react by addition of acetic acid to give the isomeric esters. When the decomposition was performed in the presence of anthracene, the aryne adduct, 1-t-butyl-triptycene was formed. The nitrosamide was thought to rearrange to the cis- rather than the trans-diazoester on the grounds of the large steric repulsion of the t-butyl group. Later work by



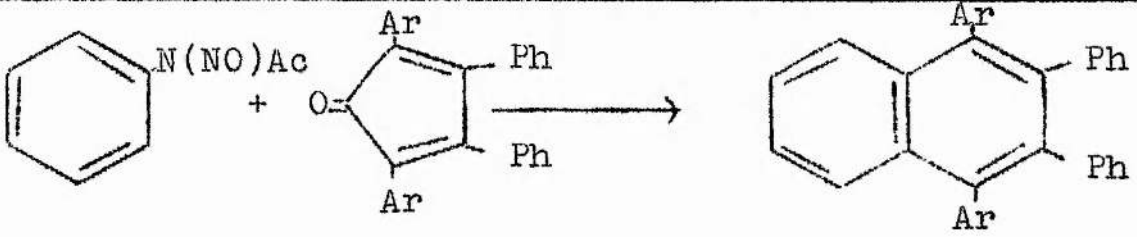
Cadogan and his co-workers led to a modification of this theory as will be discussed later.

Cadogan et al.[66,80,81] later showed that this remarkable formation of aryne adducts was not restricted to o-t-butyl-N-nitrosoacetanilide alone, and that formation of 1,2,3,4-tetraphenylnaphthalenes from the reactions of acylarylnitrosamines, including

N-nitrosoacetanilide itself, with 2,3,4,5-tetraphenylcyclopentadienone in yields up to 80% was possible, and their results are summarised in the Introduction (pp. 28,29). The results of this investigation (Tables 16 and 17) have shown that in addition to reacting with 2,3,4,5-tetraarycyclopentadienones, N-nitrosoacetanilide will also react with the anthracene nucleus to give triptycenes in yields up to 30%. The yield of adduct was found to be highest when an electron releasing group was present in the arynophile.

TABLE 16

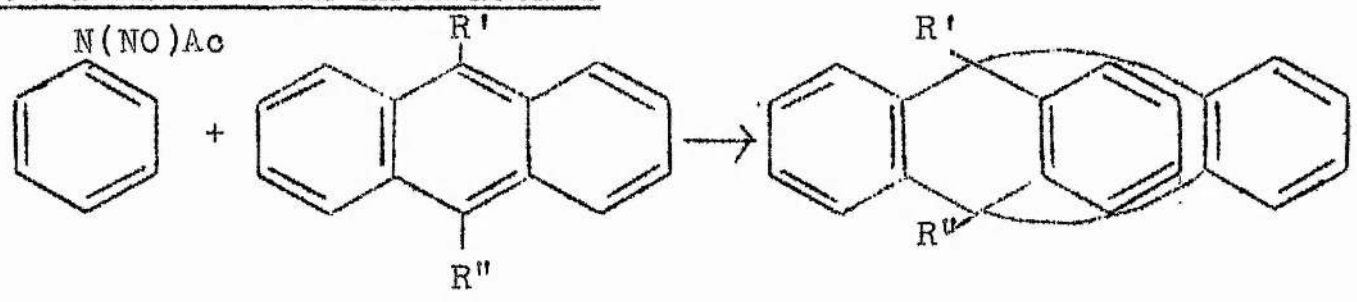
Yield of adducts from the reactions of N-nitrosoacetanilide with 2,3,4,5-tetraarylcyclopentadienones



Ar	Solvent	Yield (m/100m)
Ph	Benzene	22.0
Ph	Furan	1.4
Ph	Acetic acid	4.0
Ph	Bromotrichloromethane	25.0
p-$MeOC_6H_4$	Benzene	82.0
p-MeC_6H_4	Benzene	82.0
p-$MeSO_2C_6H_4$	Carbon tetrachloride	19.0

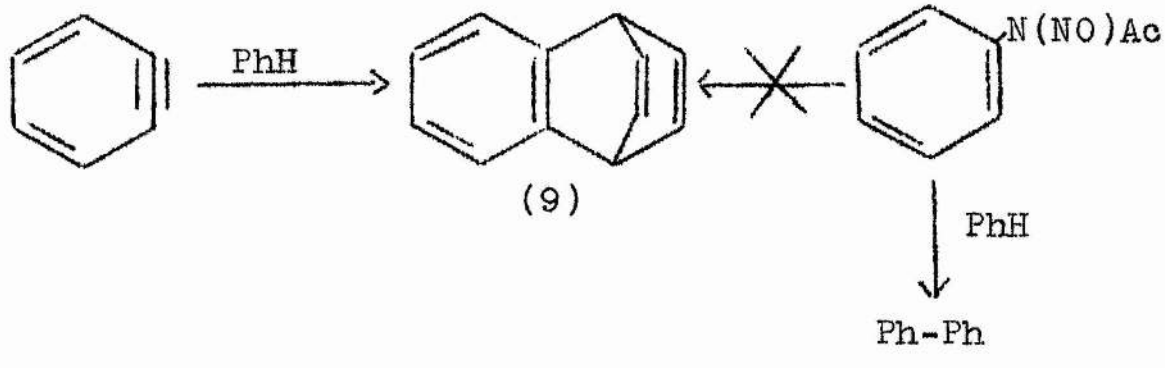
TABLE 17

Yields of adducts from the reactions of N-nitroso-acetanilide with anthracenes

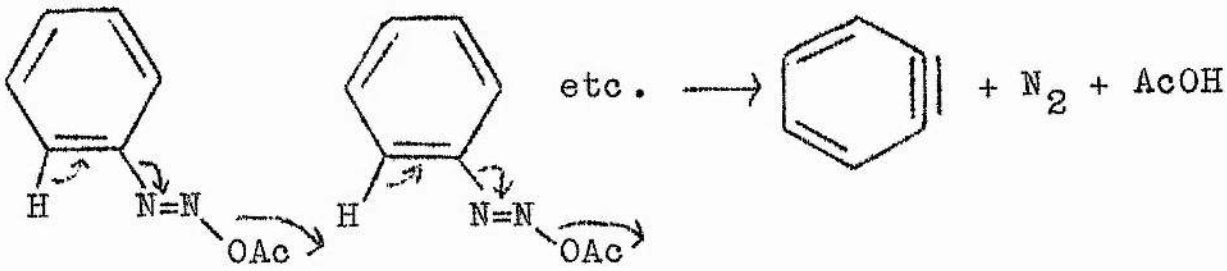


R'	R"	Solvent	Yield (m/100m)
H	H	Benzene	5.0
CH_3	CH_3	Benzene	30.0
OCH_3	OCH_3	Benzene	15.0
Br	H	Benzene	4.0
NO_2	H	Benzene	7.0

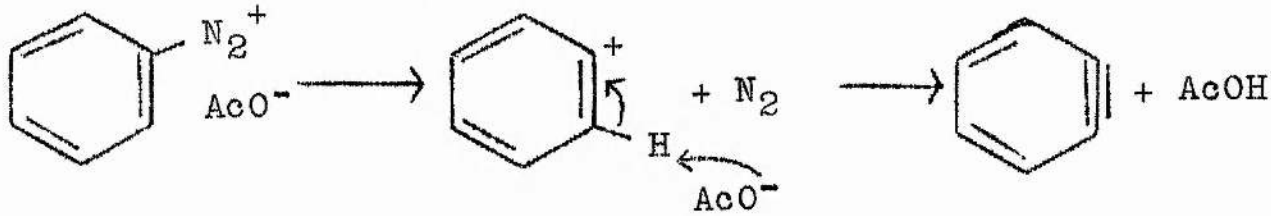
Although benzene itself has been shown to act as an arynophile [99] to give benzobicyclo[2,2,2]octatriene (9); reaction of N-nitrosoacetanilide with benzene gave only biphenyl (43%). (0.2% of (9) would have been detected).



Cadogan and Hibbert [79], in 1964, saw the formation of 3-t-butylbenzyne from the decomposition of o-t-butyl-N-nitrosoacetanilide in benzene as being due to rearrangement to the cis-, rather than the trans-diazoester; while it is possible to write an analogous scheme for N-nitrosoacetanilide, it has to be borne in mind that Huisgen [58 (d,e)] has shown that it is the trans-, and not the cis-diazoacetate which is formed in this case. Two alternatives present themselves; first, the formation of benzyne via an intermolecular reaction between molecules of the trans-diazoacetate; or second, by abstraction of the ortho-

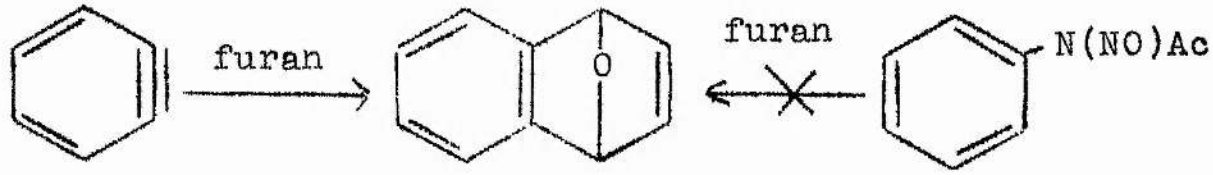


hydrogen of the phenyl carbonium ion:

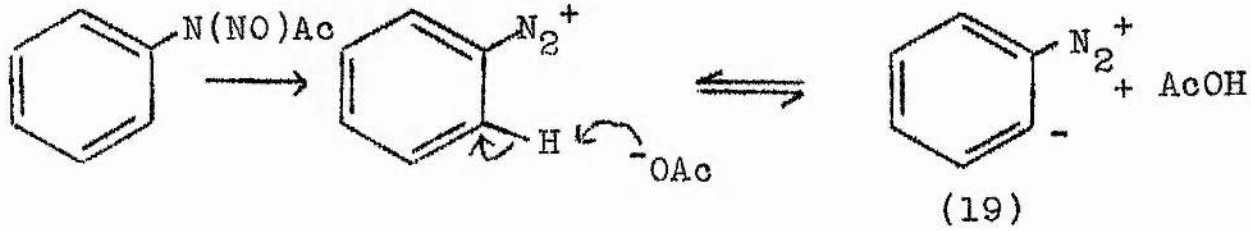


In the reaction of N-nitrosoacetanilide with furan, it was shown by Brydon [81] that the adduct 1,4-dihydronaphthalene-1,4-endoxide was not a product of the reaction although it was shown to be stable

under reaction conditions. Benzyne, on the other hand, has been shown to form this adduct with furan [90].

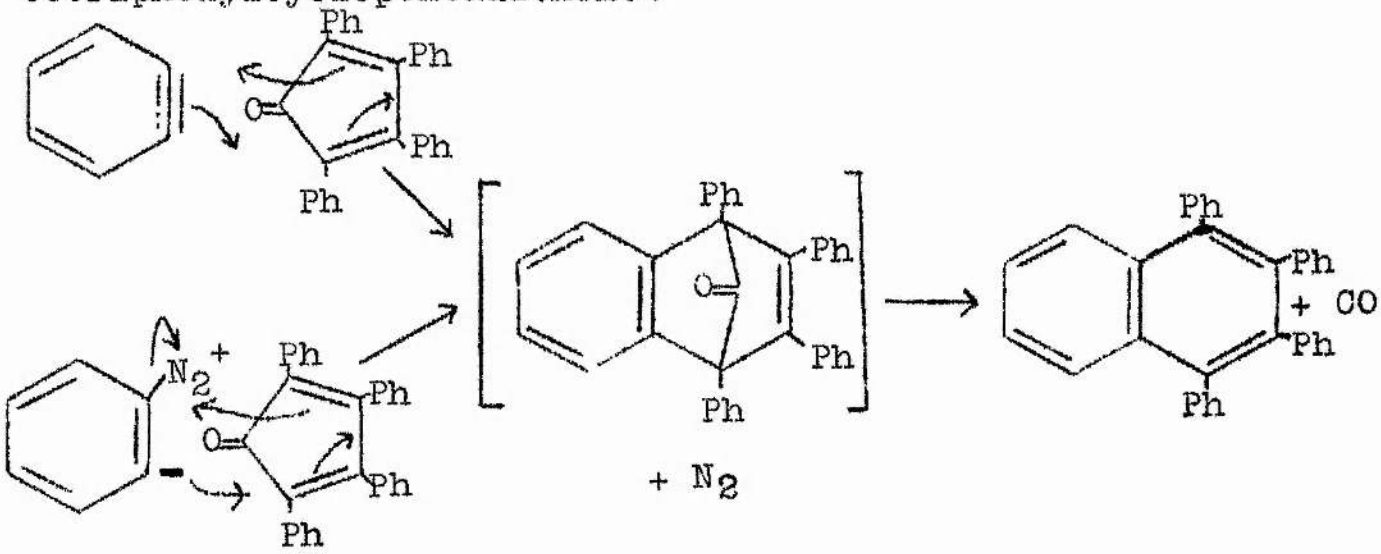


It is possible, therefore, that the intermediate leading to the formation of aryne adducts in the reactions of acylarylnitrosamines is not an aryne, and that instead an arynoid intermediate, e.g., (19) is involved:

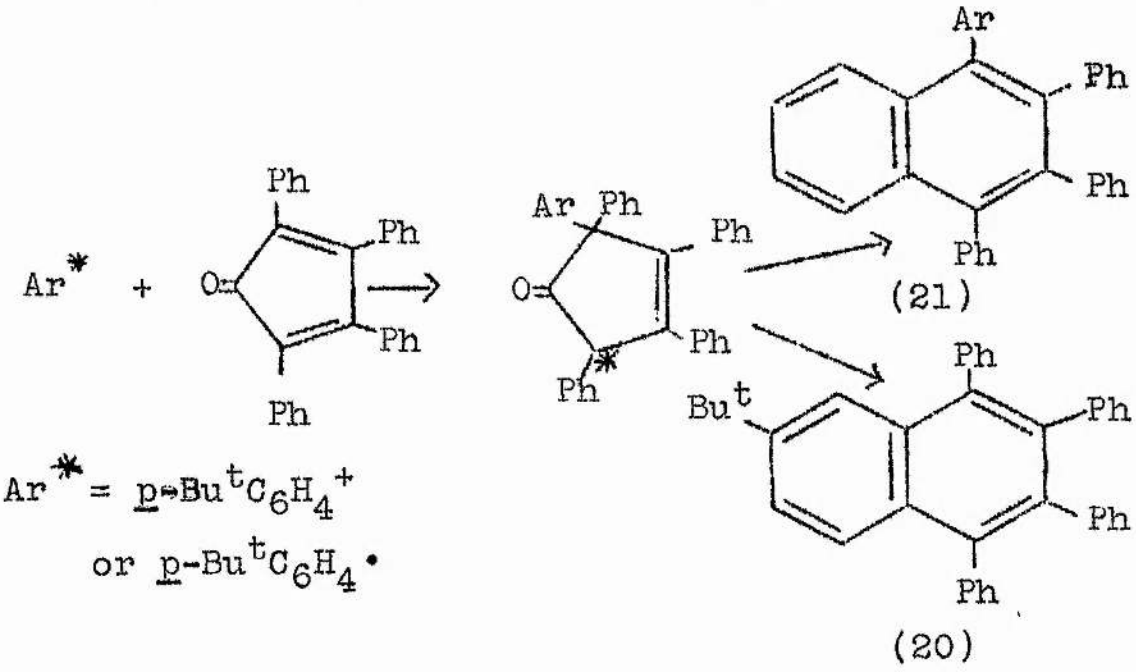


(19)

The reactions of N-nitrosoacetanilide will be discussed in terms of these two possible intermediates. For example, both can lead to the formation of 1,2,3,4-tetraphenylnaphthalene by dipolar addition to 2,3,4,5-tetraphenylcyclopentadienone:



The possibility that the intermediate leading to the formation of aryne adducts was a monodentate species, albeit free radical or carbonium ion, was ruled out by the recent results of Cadogan et al.[157]. They have shown that whereas the decomposition of p-t-butyl-N-nitrosoacetanilide in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone via addition of a monodentate species to the diene, would give 6-t-butyl-1,2,3,4-tetraphenylnaphthalene (20) and the isomeric 1-(p-t-butylphenyl)-2,3,4-triphenylnaphthalene (21), only (20) was formed in practice.



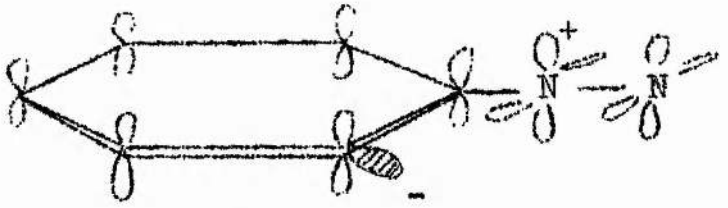
Ar^{*} = p-$Bu^{t}C_6H_4^{+}$
or p-$Bu^{t}C_6H_4\cdot$

(21)

(20)

From Tables 16 and 17, we see the preference of the intermediate in the decomposition of N-nitroso-acetanilide for an electron rich diene. This need not be evidence in favour of benzyne rather than the

benzynoid intermediate, for although benzyne is known to be electrophilic, it would seem likely on looking more closely at the structure, that (19) would indeed also be electrophilic. If we imagine (19)



(19)

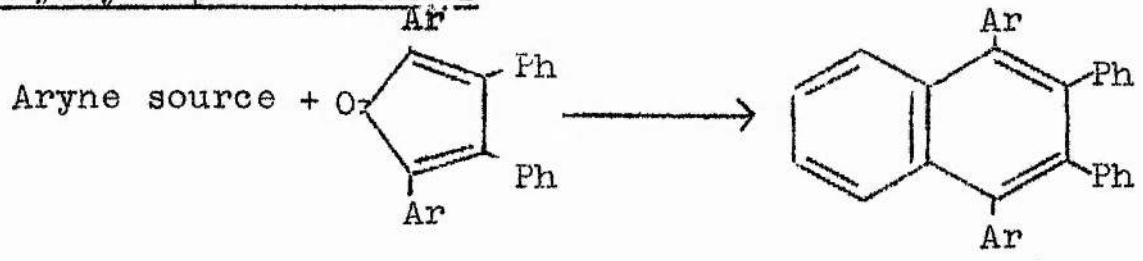
to be formed by removal of the ortho-proton, the remaining electron pair is localised in an orthogonal orbital. The interaction between this sp^2 orbital and the π-orbitals of the ring will be weak, whereas the electron deficient π-orbitals of nitrogen can easily overlap with the π-orbitals of the ring to give a degree of electrophilicity.

It was necessary, therefore, to design experiments in which not only the electrophilicity of the intermediate in the decomposition of N-nitrosoacetanilide could be tested, but also its reactivity. Competition reactions were performed in which N-nitrosoacetanilide was allowed to react with an excess of an equimolar mixture of two arynophiles, and the competition constant K_2^1, where K_2^1 = moles of adduct 1/moles of adduct 2, was measured for a series of mixtures of 2,3,4,5-tetra-

arylcyclopentadienones and anthracenes. The results were then compared with the results of similar reactions of the authentic benzyne sources pentyl nitrite/anthranilic acid and 1-aminobenzotriazole/lead tetraacetate. It was found that both N-nitrosoacetanilide and authentic benzyne lead to formation of adducts at the same rate (Table 18).

TABLE 18

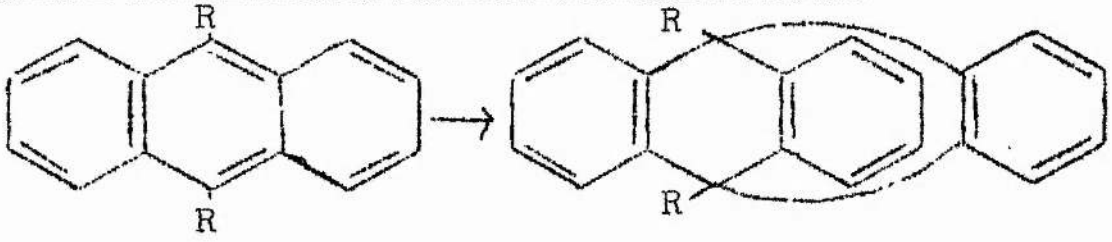
Competition reactions using pairs of 2,3,4,5-tetraarylcyclopentadienones



Arynophile pair	Solvent	NNA PN/AA AB
Ar = p-MeC_6H_4, p-$MeOC_6H_4$	Benzene	K^{OMe}_{Me} = 1.0 , 1.0 , 1.0
p-MeC_6H_4, p-$MeOC_6H_4$	Carbon tet.	K^{OMe}_{Me} = 1.0 , 1.0
p-$MeOC_6H_4$, p-$MeSO_2C_6H_4$	Carbon tet.	$K^{OMe}_{SO_2Me}$ = 2.2 , 2.1

Abbreviations used are NNA (N-nitrosoacetanilide), PN/AA (pentyl nitrite/anthranilic acid), and AB (lead tetraacetate/1-aminobenzotriazole).

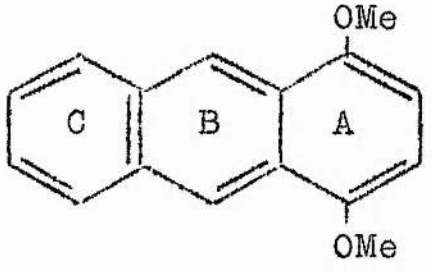
Competition reactions using pairs of anthracenes

Aryne source + 

Arynophile pair	Solvent	NNA	NNA	PN/AA
R = OMe, H	Benzene	K_H^{OMe} = 3.2 ,		3.1
R = Me, H	Benzene	K_H^{Me} = 19.7 ,		19.5

After this portion of the work had been completed and a preliminary report submitted for publication, Klanderman and Criswell [96] confirmed the greater reactivities towards benzyne of 9,10-dimethoxyanthracene and 9,10-dimethylanthracene compared with anthracene, and obtained K_H^{OMe} and K_H^{Me} values of 2.7 and 19.2 respectively.

Klanderman and Criswell have also shown [95] that in the reaction of benzyne with 1,4-dimethoxyanthracene the ratio of B-ring adduct to A-ring adduct formed is independent of the benzyne precursor. They obtained values of 2.1 - 2.6 for a series of benzyne precursors. (For formulation of adducts, see p. 34).

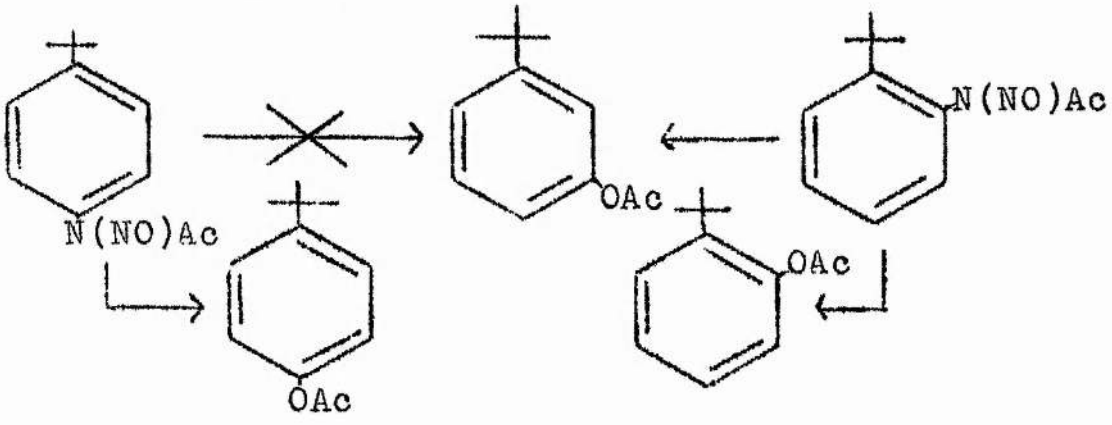
Benzyne source +  ⟶ A-ring adduct + B-ring adduct

In the present investigation, the value obtained for the ratio of B-ring adduct to A-ring adduct in the reaction of N-nitrosoacetanilide with 1,4-dimethoxyanthracene in benzene was 2.6, as was that of a similar reaction using pentyl nitrite and anthranilic acid.

The results of these competition reactions would point to the intermediacy of true benzyne were it not for three complicating factors discovered during the course of this investigation.

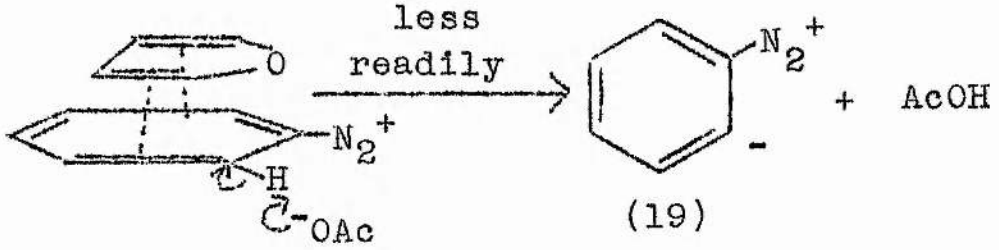
First, N-nitrosoacetanilide does not form an adduct with the strong arynophile furan [81]; and formation of 1,2,3,4-tetraphenylnaphthalene from the reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in mixtures of furan and benzene is reduced from 22% in pure benzene gradually to 1.4% in pure furan. (See figure 1, opp. p. 108). Second, no cine substitution products were detected in the reactions of acylarylnitrosamines, except in the case of o-t-butyl-N-nitrosoacetanilide.

e.g.,



Third, as described in more detail below, the reaction of N-nitrosoacetanilide with dimethylacetylenedicarboxylate in benzene leads to the formation of 1,2,3,4-tetracarbomethoxynaphthalene as a major product, whereas the reaction of authentic benzyne from pentyl nitrite and anthranilic acid gave only 5,6,11,12-tetracarbomethoxydibenzo[a,e]cyclooctatetraene.

Figure 1 (opp. p. 108) shows the effect addition of furan has on the yield of 1,2,3,4-tetraphenylnaphthalene formed in the reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in benzene. It was thought that the effect of furan was to stabilise the benzyne precursor, i.e., the diazonium cation, via π or σ-donation, resulting in reduced acidity of the ortho-hydrogen. Brydon [81],

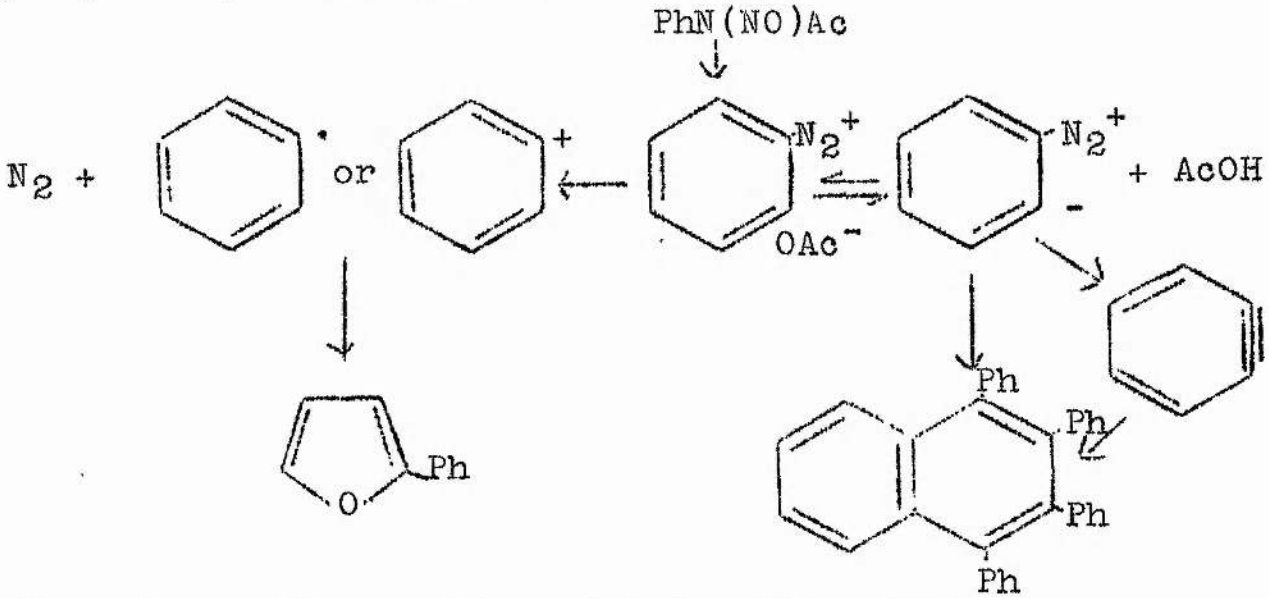


(19)

however, showed that the reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in tetrahydrofuran lead to the formation of 1,2,3,4-tetraphenylnaphthalene in 24% yield, so the possibility of stabilisation by σ-donation at least, can be ruled

out. Koller and Zollinger [158] have shown that diazonium salts form π-complexes in dilute acetic acid with naphthalene and 1-methylnaphthalene, but noted that the electrophilicity of the diazonium group was reduced only slightly; and it seems that formation of such a π-complex between the diazoacetate and furan is the best explanation of the reduction in yield of benzyne adduct.

Figure 1 (opp. p. 108) shows that the fall in yield of 1,2,3,4-tetraphenylnaphthalene is matched exactly by the increase in yield of 2-phenylfuran. This would suggest that the addition of furan altered the balance between an aryne adduct-forming, and a phenylating intermediate. π-Stabilisation of the

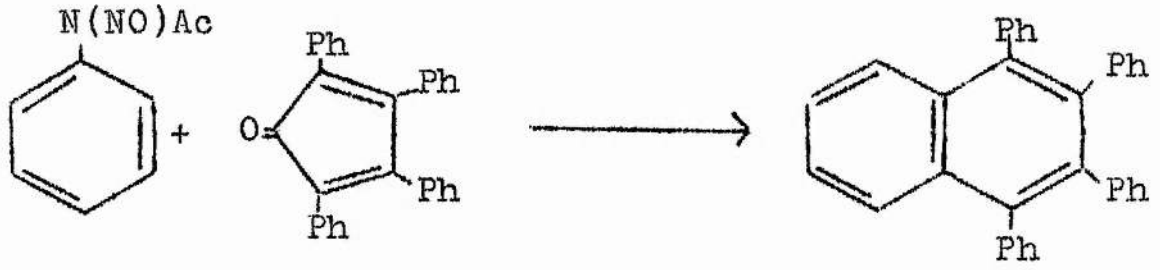


diazonium cation would certainly alter this balance, since formation of the phenylating species, albeit radical or carbonium ion, is an irreversible

process.

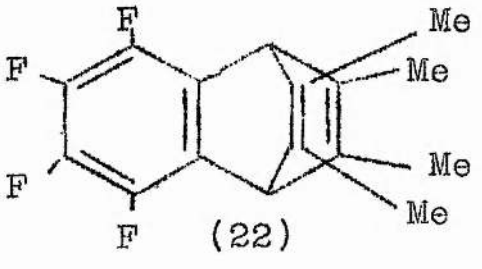
It was thought that the known electron rich systems of durene and hexamethylbenzene might exhibit the same behaviour as furan, but instead of reducing the yield of 1,2,3,4-tetraphenylnaphthalene, it was increased by some 10%, and the durene and hexamethylbenzene recovered quantitatively. (Table 19).

TABLE 19

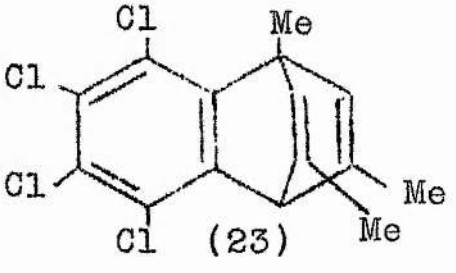


Solvent	Yield (%)
Benzene	22.0
Benzene/durene	34.0
Benzene/hexamethylbenzene	33.0

Polymethyl compounds have been shown to be reactive towards electrophilic arynes; Callander, Coe and Tatlow [159] have shown that tetrafluorobenzyne gives an aryne adduct (22) with durene. Similarly Heaney



(22)



(23)

and Jablonski [160] have isolated (23) from the reaction of tetrachlorobenzyne with mesitylene. It is possible, therefore, that the effect of addition of durene or hexamethylbenzene in the reaction of N-nitrosoacetacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in benzene is to stabilise the intermediate benzyne or benzynoid intermediate rather than their precursor.

The second problem associated with the postulation of a benzyne rather than a benzynoid species is the lack of cine substitution products from the reactions of substituted acylarylnitrosamines (Table 20).

TABLE 20

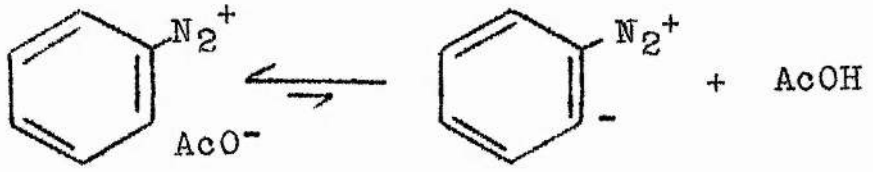
Formation of acetates in the reactions of acylarylnitrosamines

$RC_6H_4N(NO)Ac \longrightarrow RC_6H_4OAc$

	Solvent	Yield (%)		
		ortho	meta	para
R= p-OMe	CH_2Br_2	-	0	0
p-COOEt	CH_2Br_2	-	0	16.7
p-NO_2	$BrCCl_3$	-	0	3.4
m-Br	$BrCCl_3$	0	11.2	0
o-Bu^t	$BrCCl_3$	45.0	16.5	0
*p-Bu^t	PhH	-	0	0.5

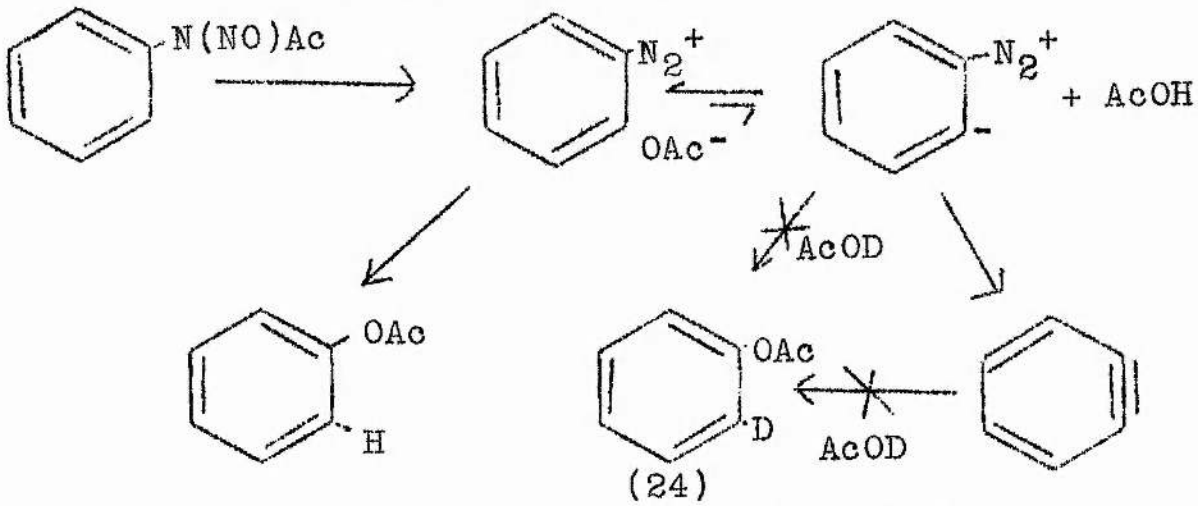
*Result obtained by Dr.M.J.P.Harger.

The reaction of N-nitrosoacetanilide with acetic acid provided some interesting results. In the presence of 2,3,4,5-tetraphenylcyclopentadienone, the major product was phenyl acetate, with only 4% of 1,2,3,4-tetraphenylnaphthalene formed. The latter can be explained in terms of a shift in the diazonium ion-arynoid equilibrium caused by the excess of acetic acid.



In the absence of 2,3,4,5-tetraphenylcyclopentadienone, DeTar [56] has shown that the major product, in acetic acid as medium, was again phenyl acetate (50%). If the formation of acetates in the reactions of acylarylnitrosamines was via addition of acetic acid to the intermediate aryne, decomposition of N-nitrosoacetanilide in deuteroacetic acid would lead to deuterium incorporation in the product. In the case of postulation of (19) as the arynoid species, this too would be expected to lead to dueterium incorporation. Examination of the ester formed when this reaction was carried out showed no M^+ value attributable to o-deuterophenyl acetate (24),

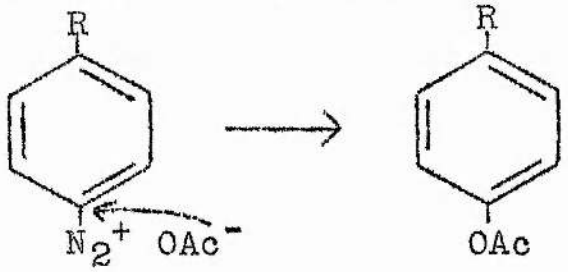
0.1% would have been detected, and the i.r. and n.m.r. spectra were indistinguishable from those of phenyl acetate. It is possible, however, that because of the unfavourability of the equilibrium towards



(24)

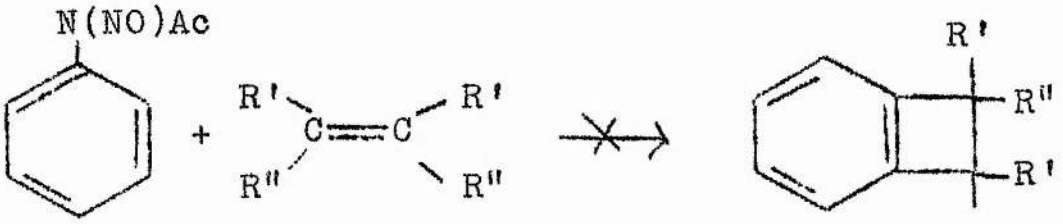
formation of the aryne or arynoid species (19), the formation of phenyl acetate would be preferred to the formation of (24). The formation of acetates in the decomposition of acylarylnitrosamines, in both benzene and halogenated solvents, may also be via an intramolecular reaction, thus leading to the formation of only one ester.

e.g.,



The special case of o-t-butyl-N-nitroso-acetanilide, which gives cine substitution, will be discussed later.

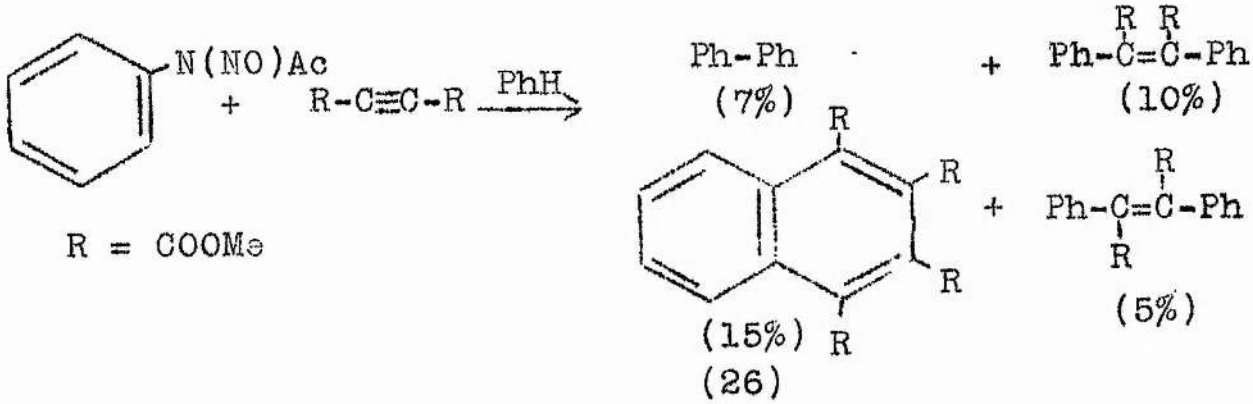
The apparent conflict between the benzyne and the benzynoid theories led to further experiments in which addition of the intermediate from N-nitrosoacetanilide to double and triple bond systems was attempted. Reaction of N-nitrosoacetanilide with both diethyl maleate and tetracyanoethylene in benzene did not lead to the formation of the substituted benzocyclobutanes (25 a,b), but gave biphenyl as the



(a) R' = H, R" = COOEt (25)

(b) R' = R" = CN

only product, along with a quantitative recovery of the alkene. The reaction of N-nitrosoacetanilide with acrylonitrile in benzene gave only polymeric material. Reaction with dimethylacetylenedicarboxylate in benzene, however, gave cis-, and trans-dimethyl diphenylmaleate and 1,2,3,4-tetracarbomethoxynaphthalene (26) along with the expected biphenyl.

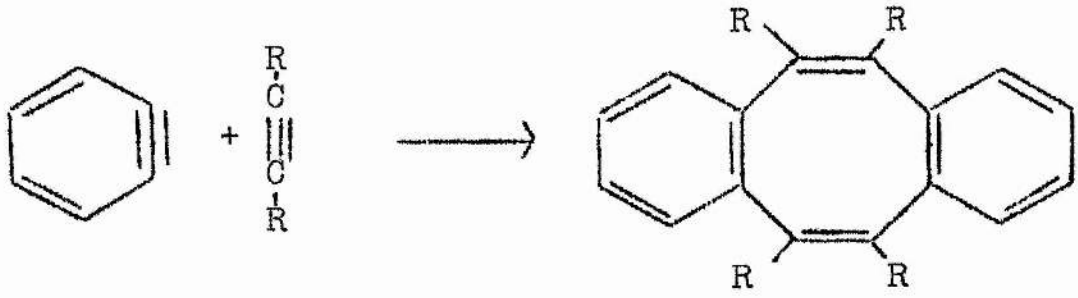


R = COOMe

Ph-Ph (7%) + Ph-C(R)=C(R)-Ph (10%)

(15%) (26) + Ph-C(R)=C(R)-Ph (5%)

These products were not formed, however, in the reaction of authentic benzyne with dimethylacetylenedicarboxylate in benzene, which gave only 5,6,11,12-tetracarbomethoxydibenzo[a,e]cyclooctatetraene (27). This

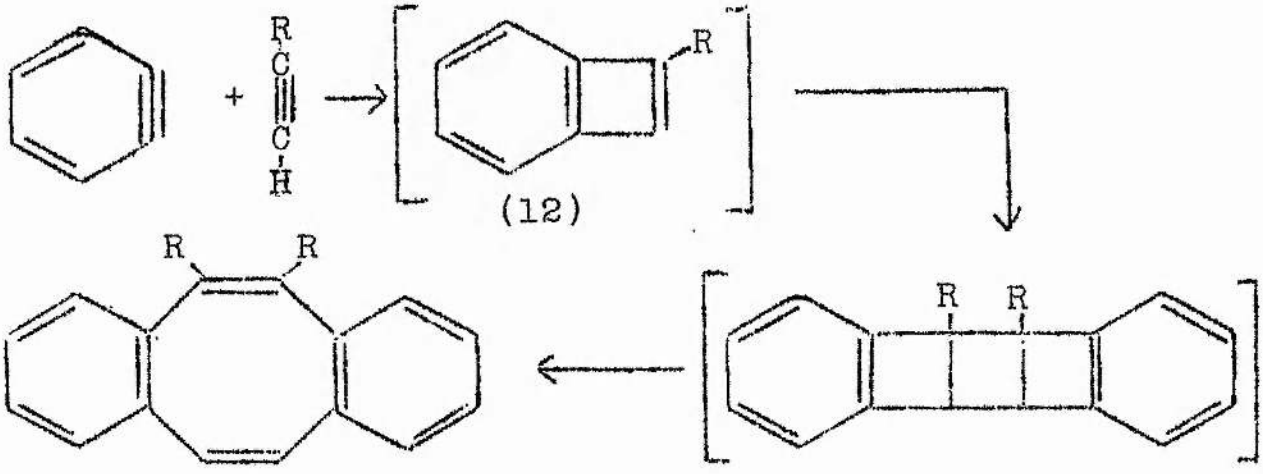


R = COOMe

3%

(27)

latter reaction is analogous to the reaction of benzyne with methyl propiolate, which has been shown [101] to give 5,6-dicarbomethoxydibenzo[a,e] cyclooctatetraene (14). Formation of (14) was rationalised as being by initial formation of the benzocyclobutene (12) which then dimerised and ring-opened



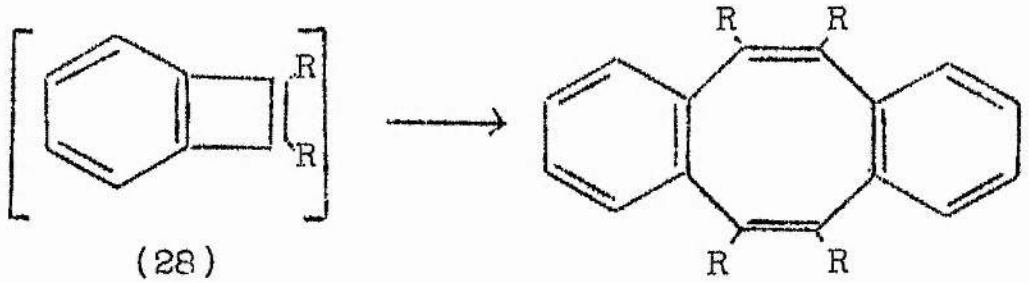
7%

(14)

R = COOMe

to give the observed product (14).

If the reaction of N-nitrosoacetanilide with dimethylacetylenedicarboxylate in benzene were via bidentate addition, either benzyne or benzynoid, the benzocyclobutene (28) would be formed. This would

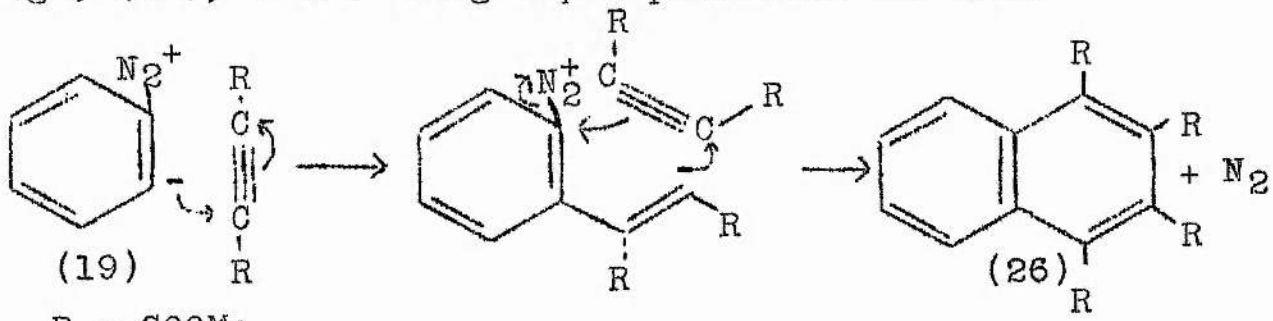


(28)

R = COOMe

(27)

then dimerise and ring open to give (27) as in the reaction of benzyne with methyl propiolate. The fact that (27) was not observed in the reaction of N-nitrosoacetanilide with dimethylacetylenedicarboxylate would imply that attack on the diester is via a monodentate rather than a bidentate species, e.g., (19), there being ample precedent for such



(19)

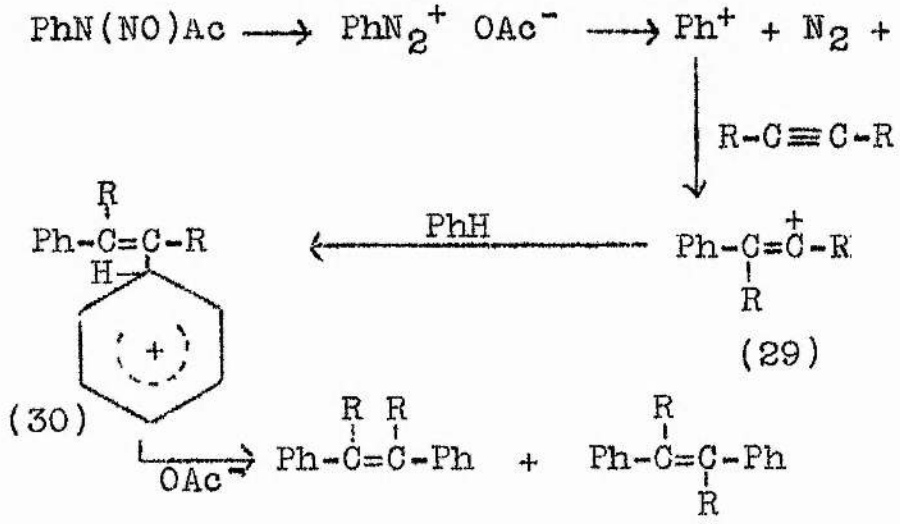
R = COOMe

(26)

stepwise addition of nucleophiles to acetylenedicarboxylates.

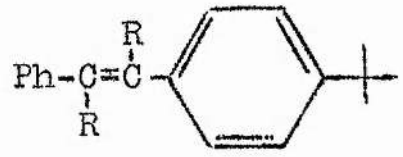
The other surprising products formed in the

reaction of N-nitrosoacetanilide with dimethylacetylenedicarboxylate in benzene were the cis-, and trans-dimethyl diphenylmaleates. These esters were not, however, products of a similar reaction with phenylazotriphenylmethane. This latter reaction gave biphenyl, triphenylmethane and a quantitative recovery of dimethylacetylenedicarboxylate, implying that N-nitrosoacetanilide reacts via an ionic rather than a free radical scheme, e.g.,



Addition of a phenyl carbonium ion to the diester would give (29), which could add to a molecule of solvent to give (30). Abstraction of a proton from (30) would then give the cis-, and trans-dimethyl diphenylmaleates. This mechanism, however, must seem unlikely in view of the electron deficiency of the triple bond system, and clearly more work

is required to elucidate the mechanism further. A similar experiment with p-t-butyl-N-nitrosoacetanilide and dimethylacetylenedicarboxylate in benzene gave inconclusive results, though in this case the yield of biaryl was high (25%) indicating the unfavourability of a more complex reaction. Apart from p-t-butyl-acetanilide (4%), the only other product isolated was an oil. This oil had the correct mass for isomers of dimethyl 1-phenyl-2-p-t-butylphenyl-maleate (31), but the analysis, (Found: C, 75.8; H,7.5. $C_{22}H_{24}O_4$ requires C, 75.0; H 6.82%), was incorrect. Repeated attempts at purification failed, and while hydrogenation of (31) would be expected



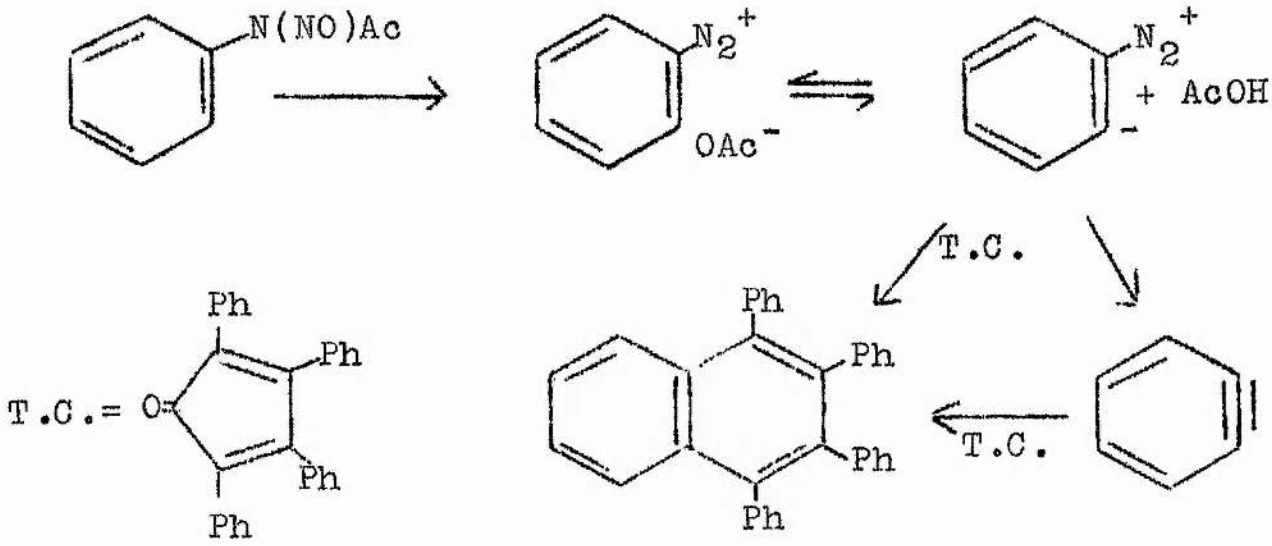
R = COOMe

(31)

to occur readily, attempted hydrogenation left the oil unchanged.

In conclusion therefore, it can be said that although N-nitrosoacetanilide leads to the formation of benzyne adducts at the same rate as authentic benzyne, it is not possible to say, on the present evidence, that the intermediate involved is actually

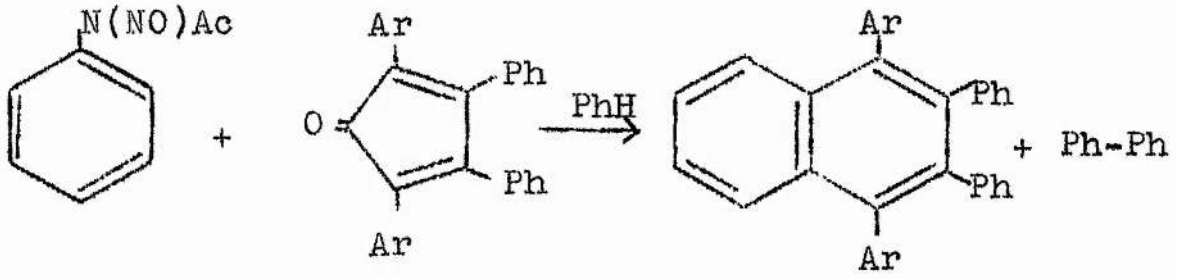
true benzyne. Both benzyne and the postulated benzynoid species (19) may lead to the formation of adducts, but since benzyne may be formed from the benzynoid species, it is clearly not possible to differentiate between which part of the adduct is formed from the one and which from the other.



The high yields of 1,4-di-p-methylphenyl-2,3-diphenylnaphthalene and 1,4-di-p-methoxyphenyl-2,3-diphenylnaphthalene , and the consequent suppression of biphenyl formation in the reaction of N-nitroso-acetanilide with 2,3,4,5-tetraarylcyclopentadienones would indicate that the formation of the benzyne adduct was at the expense of biphenyl formation. (Table 21.)

TABLE 21

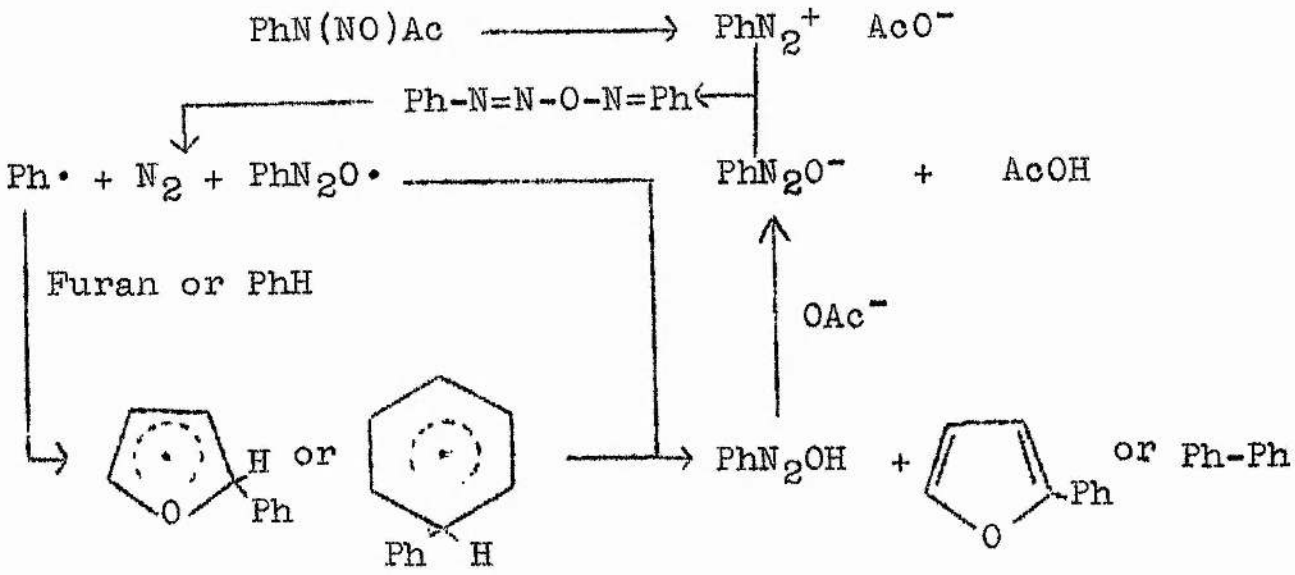
Reaction of N-nitrosoacetanilide with 2,3,4,5-tetraarylcyclopentadienones



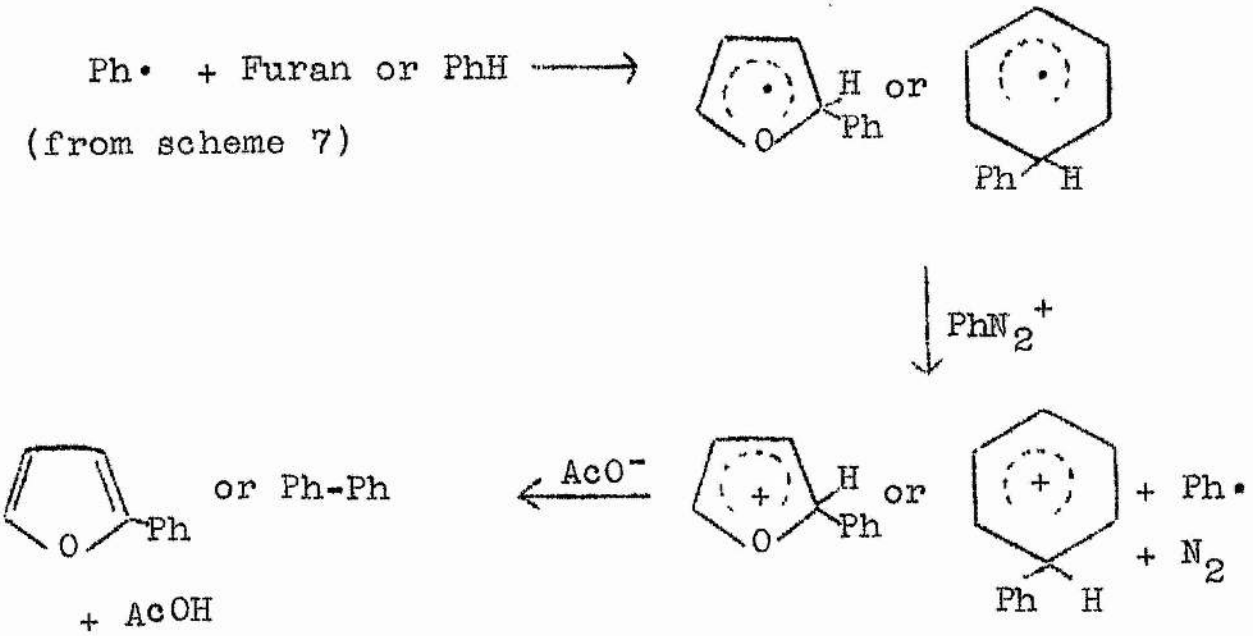
(a) Ar = Ph	22.0%	16.0%
(b) Ar = p-MeC_6H_4	82.0%	0
(c) Ar = p-$MeOC_6H_4$	82.0%	3.0%
(d) No trap	-	43.0%

This would imply a common intermediate, e.g., (19) which could alternatively give benzyne adduct or biphenyl. If this is the case, it still remains to be explained why the reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in furan leads to 2-phenylfuran (22%) as the major product. To rationalise this on the basis of the above theory, it is necessary to assume that, in addition to π-stabilisation of the benzenediazonium cation by furan, the phenylation of furan is much faster than that of benzene. Recent research results [161], though not yet completed, indicate that this may indeed be so.

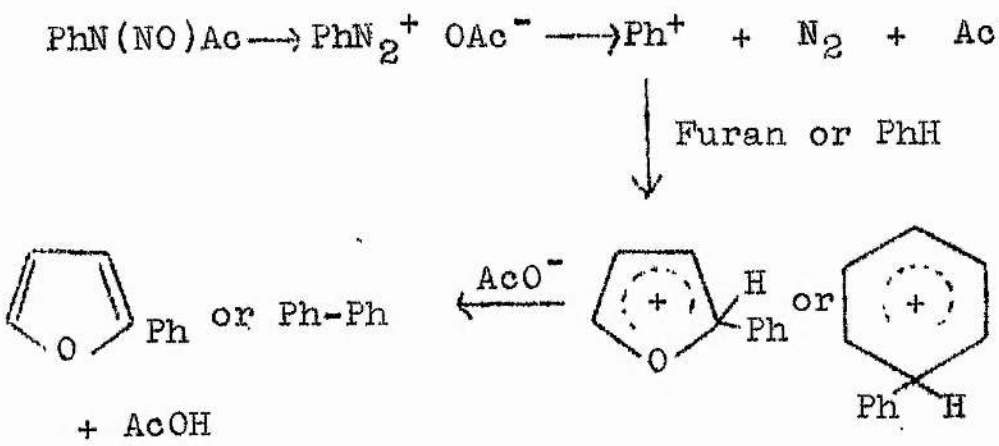
Possible mechanisms for the phenylation of furan and benzene by N-nitrosoacetanilide are shown below. (Schemes 7,8 and 9).



Scheme 7.



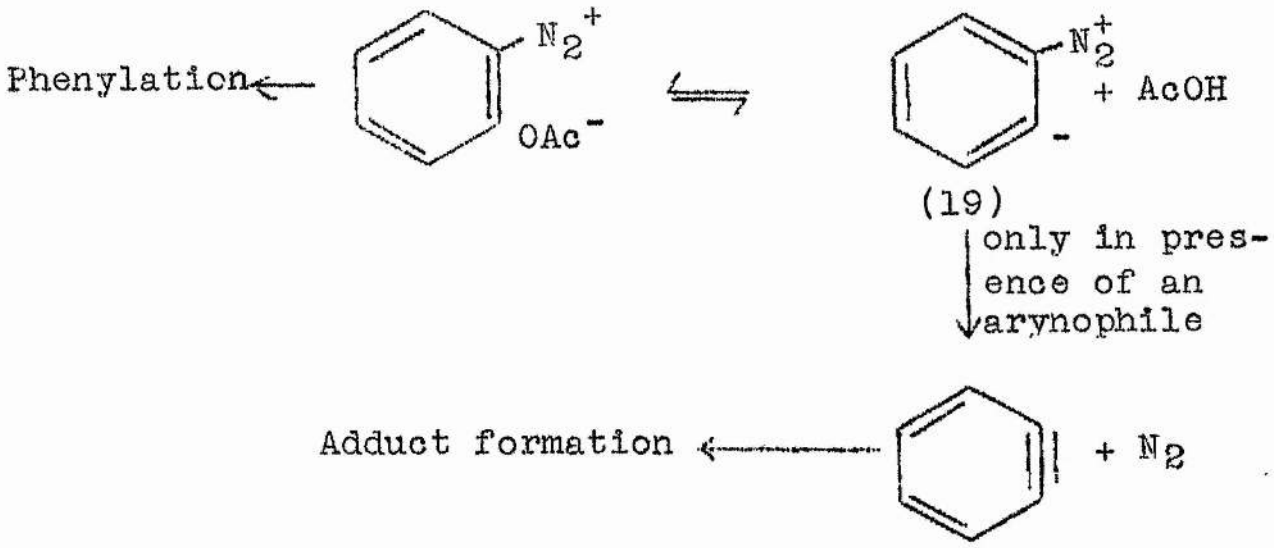
Scheme 8.



Scheme 9.

In schemes 8 and 9, the known affinity of the furan nucleus for electrophilic species may lead not only π-stabilisation, but also to a lowering of the activation energy required to reach the transition state for the redox or addition steps. This would result in an increase in reaction rate compared to reaction in benzene, for which an analogous stabilisation is less likely. If this is indeed the case, it would lead to preferential removal of the benzenediazonium cation by a route other than that leading to the benzyne or benzynoid species, thus explaining the observed suppression of aryne adduct by furan. In any event, reaction via Scheme 7 can certainly not be ruled out.

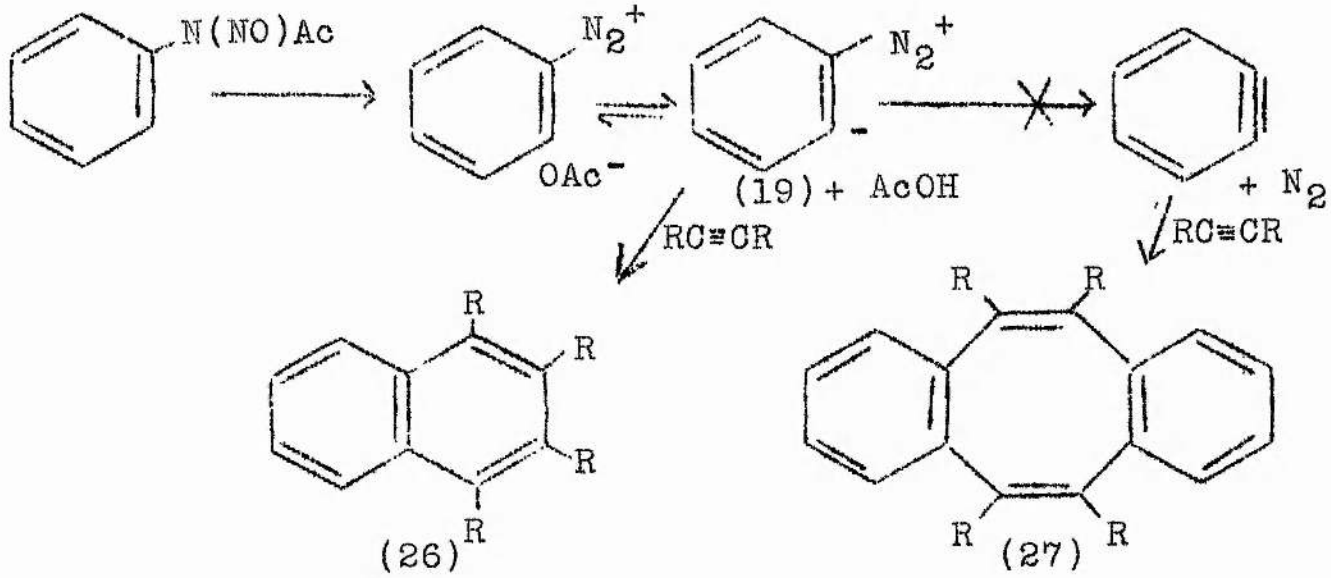
Another possibility is that (19) itself may not be an adduct forming species, and requires the presence of an arynophile to induce decomposition to benzyne.



In the absence of an arynophile, the equilibrium shifts in favour of phenylation either in furan or benzene. In the presence of an arynophile, however, decomposition of (19) to benzyne is induced, except in furan where the faster phenylation would be preferred; though this mechanism is , to say the least, speculative.

That (19) exists would seem to be true from the reaction of N-nitrosoacetanilide with dimethylacetylenedicarboxylate in benzene, which gave 1,2,3,4-tetracarbomethoxynaphthalene (26), a different adduct from a similar reaction using the authentic benzyne source pentyl nitrite and anthranilic acid, which gave (27). It may be, however, that the reaction

leading to the formation of 1,2,3,4-tetracarbomethoxynaphthalene (26) is energetically preferred, and that (19) is intercepted before it can decompose to benzyne.



Clearly, on the present evidence alone, it is not possible to resolve the problem of benzyne or benzynoid participation. Although this latter experiment provides good evidence for the participation of the benzynoid species (19), is it reasonable to assume that it would have the same reactivity towards arynophiles as authentic benzyne? More research work is therefore required to take this argument further.

III The reaction of acylarylnitrosamines with halogenomethanes

Boeseken and Gelissen [16,17] and Wieland [19] showed that the reaction of the free radical sources dibenzoyl peroxide and phenylazotriphenylmethane with carbon tetrachloride gave chlorobenzene together with hexachloroethane and 1,1,1-trichloro-2,2,2-triphenylethane.

$$Ph\cdot + CCl_4 \longrightarrow PhCl + CCl_3\cdot \begin{cases} \nearrow CCl_3\text{-}CCl_3 \\ \searrow CCl_3\text{-}CPh_3 \end{cases}$$

While the mechanism for the decomposition of N-nitrosoacetanilide was thought to involve an analogous free radical process, the absence of hexachloroethane from the reaction of N-nitrosoacetanilide with carbon tetrachloride was noted by several workers [6,20]. Further anomalous behaviour was observed by Hey and Peters [20] who showed that while the reactions of dibenzoyl peroxide and phenylazotriphenylmethane with both chloroform and carbon tetrachloride led to the formation of only chlorobenzene, N-nitrosoacetanilide gave chlorobenzene with carbon tetrachloride, but both benzene and chlorobenzene with chloroform. Although these

surprising results were obtained before the advent of g.l.c., they were fully confirmed by Hibbert [22] when the technique becam available.

The results of the present investigation have shown that acylarylnitrosamines, in general, behave differently from authentic radical sources in every halogenomethane studied.

A The reaction of N-nitrosoacetanilide with bromotrichloromethane

The reaction of N-nitrosoacetanilide with bromotrichloromethane at 50° led to the formation of bromobenzene, chlorobenzene and phenyl acetate,

$$PhN(NO)Ac \longrightarrow \underset{22.9\%}{PhBr} + \underset{14.6\%}{PhCl} + \underset{16.0\%}{PhOAc}$$

whereas the reaction of the authentic phenyl radical source phenylazotriphenylmethane led to the formation of only bromobenzene[22]. An additional feature presented itself in the reaction of N-nitrosoacetanilide, in that when the reaction was carried out at 15°, the nitrosamide dissolved, and after a few minutes a precipitate was observed. Examination of this precipitate showed that it had an i.r. spectrum almost identical to that of benzenediazonium chloride. In addition however, several absorptions unattributable to benzenediazonium chloride, notably one at 1720 cm^{-1},

were present.

Grieve and Hey[6] had noted, without comment in their classic paper in 1934, that the reaction of N-nitrosoacetanilide with carbon tetrachloride at room temperature gave chlorobenzene, nitrogen, and precipitated benzenediazonium chloride. The result obtained with N-nitrosoacetanilide and bromotrichloromethane seemed to parallel their result.

Halogen analysis of the precipitated diazonium salt showed that it consisted of 79% benzenediazonium chloride, but not bromide (0.2% would have been detected). That the remaining 21% consisted of benzenediazonium acetate, was shown by the diazonium and acetate absorptions in the i.r. spectrum, and by the fact that subsequent decomposition of this precipitate in fresh bromotrichloromethane led to

$$PhN(NO)Ac \xrightarrow[15^{o}]{BrCCl_3} \left.\begin{matrix} PhN_2^+\ Cl^- \\ PhN_2^+\ OAc^- \end{matrix}\right\} \xrightarrow[50^{o}]{BrCCl_3} \underset{15.8\%}{PhCl} + \underset{3.1\%}{PhBr} + \underset{6.0\%}{PhOAc}$$

the formation of phenyl acetate, as well as chlorobenzene and bromobenzene. In a control experiment, authentic benzenediazonium chloride was shown to give chlorobenzene and bromobenzene. Although this

$$PhN_2^+\ Cl^- \xrightarrow{BrCCl_3} PhCl + PhBr$$

control experiment was non-quantitative in nature, the K_{Cl}^{Br} ratio was $\fallingdotseq$ 0.3.

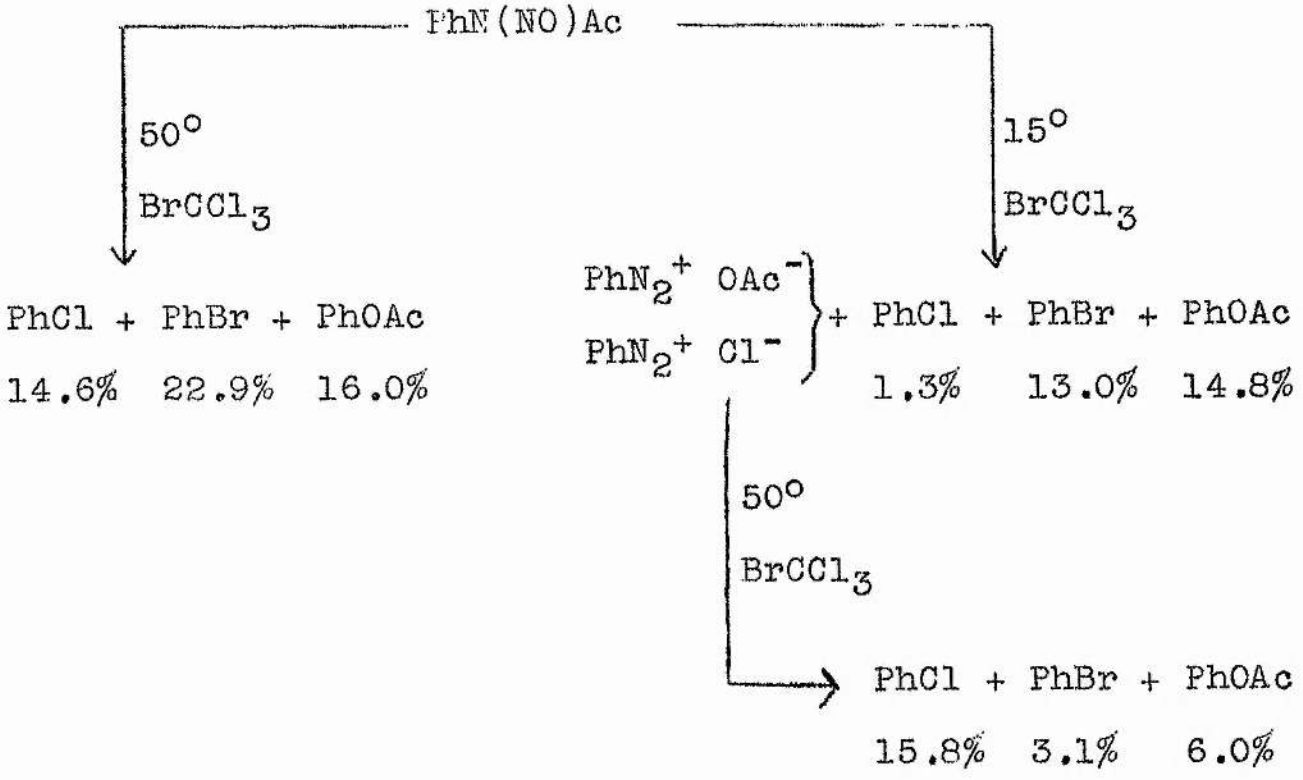
It was thus possible to perform the decomposition in two ways. First, N-nitrosoacetanilide was allowed to decompose in bromotrichloromethane at 50° and the solution analysed. Second, N-nitrosoacetanilide was allowed to decompose in bromotrichloromethane at 15°, the diazonium salt filtered, and the mother liquor analysed. The filtered diazonium salt was then allowed to decompose in fresh bromotrichloromethane at 50° and the solution analysed. The combined results are shown in Table 22.

TABLE 22

Reaction of N-nitrosoacetanilide with bromotrichloromethane

Product	Yield (%)		
	NNA/15°	Diazonium salt/50°	NNA/50°
Chlorobenzene	1.3	15.8	14.6(11.2)
Bromobenzene	13.0	3.1	22.9(19.0)
Phenyl acetate	14.8	6.0	16.0(14.1)
K_{Cl}^{Br}	10.0 / 0.94 / 0.6		1.56(1.70)
Accountance (%)	54.0		53.5(44.3)

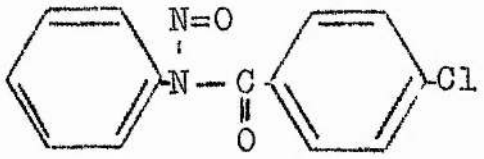
NNA = N-nitrosoacetanilide. Figures in parentheses represent results of parallel reactions. Abstraction ratio K_{Cl}^{Br} = moles PhBr/moles PhCl.



Both the stepwise reaction and the reaction at 50° gave the same overall accountance (54.0% and 53.5%). Similarly the abstraction ratio for the stepwise reaction overall is 0.94 compared with 1.56 for the reaction at 50°. The abstraction ratios for the individual stages of the stepwise reaction , however, vary from 10.0 for the reactio at 15°, to 0.6 for the subsequent decomposition of the diazonium salt in bromotrichloromethane. These results are consistent with the formation of benzenediazonium chloride and benzenediazonium acetate in the first step.

Results obtained from the reaction of 4-chloro-N-nitrosobenzanilide with carbon tetrachloride at

15° also support the intermediacy of precipitated diazoesters and chlorides in these reactions. Thus



$$\xrightarrow{CCl_4} PhN_2^+ Cl^- + PhN_2^+ OCOC_6H_4Cl^- + p\text{-}ClC_6H_4COOH$$

the decomposition of 4-chloro-N-nitrosobenzanilide in carbon tetrachloride at room temperature after 12 hr, afforded a precipitate which contained 16% benzenediazonium chloride, the remainder being a mixture of benzenediazonium p-chlorobenzoate and p-chlorobenzoic acid. On filtering a similar reaction after only 30 min, the precipitate contained rather less benzenediazonium chloride (9.3%), along with benzenediazonium p-chlorobenzoate and p-chlorobenzoic acid.

These results differ from those of Ruchardt et al.[77,78] who have isolated only benzenediazonium p-chlorobenzoate from the reaction of 4-chloro-N-nitrosobenzanilide after 30 min. Our results are supported by a similar observation by Thomson [66], who has shown that the decomposition of 4'-bromo-4-chloro-N-nitrosobenzanilide in carbon tetrachloride at room temperature, gave p-bromobenzenediazonium chloride and p-chlorobenzoic acid after a few minutes.

The mechanism for the reaction of N-nitroso-acetanilide with bromotrichloromethane, therefore, clearly involves major participation of diazonium salts, and is not a straightforward free radical reaction.

Recent e.s.r. work by Paton [67] has shown that the signal observed by Ruchardt and Freudenberg[68] in the reaction of N-nitrosoacetanilide with benzene, later identified as the PAPN radical (4) was absent in bromotrichloromethane and carbon tetrachloride. A weak signal, a 1:1:1 triplet of 1:1:1 triplets, however was observed. This was the same signal observed in addition to that due to (4) in the decomposition of N-nitrosoacetanilide in benzene, and attributed by Cadogan, Paton and Thomson [74] to the trans-phenyldiazotate radical (Ph-N=N-O•). Although no signal attributable to (4) was observed in either bromotrichloromethane or carbon tetrachloride, Paton [67] has suggested that this radical may be formed, but is scavenged immediately by a trichloromethyl radical.

$$Ph\bullet + CCl_4 \longrightarrow PhCl + CCl_3\bullet$$

$$Ph\bullet + PhN(NO)Ac \longrightarrow \underset{\underset{Ph-N-Ac}{|}}{Ph-N-O\bullet} \xrightarrow{CCl_3\bullet} \underset{\underset{Ph-N-Ac}{|}}{Ph-N-OCCl_3}$$

(4)

In methylene chloride, a weak signal due to (4) was

observed, which might be expected in the absence of the more stable trichloromethyl radical. Thus a free radical mechanism must operate, at least to some extent, in the reaction of N-nitrosoacetanilide with bromotrichloromethane. Thomson [66] has shown that in addition to acetic acid (54%), acetic anhydride (15%) was also formed in the decomposition of N-nitrosoacetanilide in carbon tetrachloride, suggesting that in that part of the reaction which proceedsvia a radical chain process, the initiation step may be similar to that proposed by Ruchardt [68] for the reaction of N-nitrosoacetanilide with benzene:

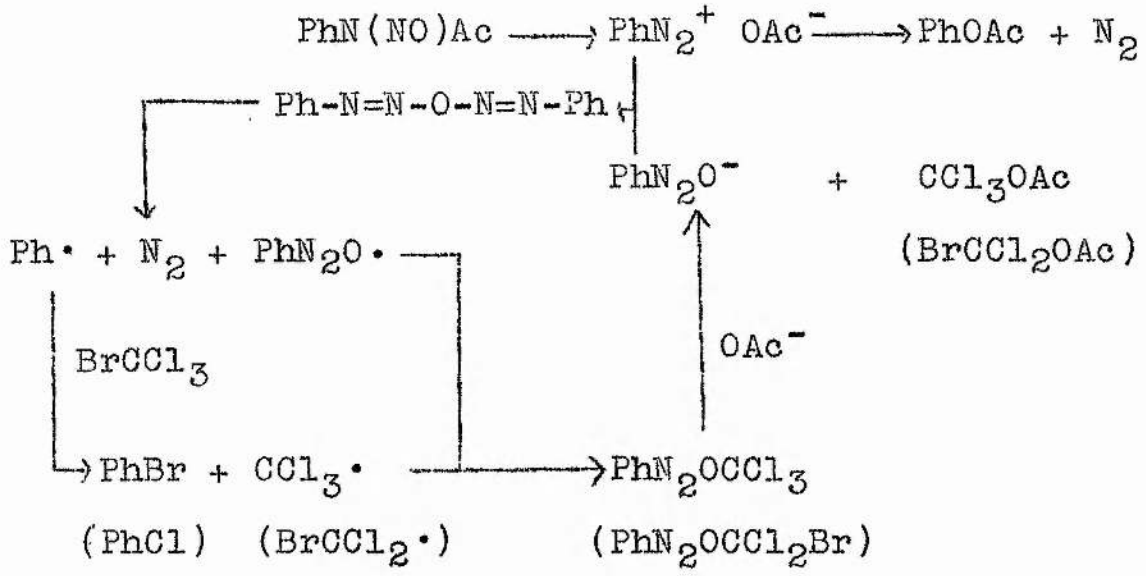
$$PhN(NO)Ac \longrightarrow Ph\text{-}N{=}N\text{-}OAc \longrightarrow PhN_2^+\ OAc^-$$

$$AcO^- + Ph\text{-}N{=}N\text{-}OAc \longrightarrow PhN_2O^- + Ac_2O$$

$$PhN_2O^- + PhN_2^+ \longrightarrow Ph\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ph \longrightarrow Ph\cdot + N_2 + PhN_2O\cdot$$

This phenyl radical could then react with bromotrichloromethane to give the observed halogen abstraction products. The modified Ruchardt mechanism is shown overleaf (Scheme 10).

The decomposition of N-nitrosoacetanilide in bromotrichloromethane via Scheme 10 would require formation of trichloromethyl acetate. Although this compound has not been isolated, reation in tetra-



Scheme 10.

chloroethane and methylene chloride would be expected

$$Ph\text{-}N{=}N\text{-}O\text{-}CCl_3 \xrightarrow{OAc^-} PhN_2O^- + CCl_3OAc$$

$$Ph\text{-}N{=}N\text{-}OCHCl\text{-}CHCl_2 \xrightarrow{OAc^-} PhN_2O^- + CHCl_2CHClOAc$$

$$Ph\text{-}N{=}N\text{-}OCH_2Cl \xrightarrow{OAc^-} PhN_2O^- + CH_2ClOAc$$

to give, by analogy, the known compounds α,β,β,-trichloroethyl acetate and chloromethyl acetate. These, however, were not detected, though the possibility that these reactive esters are consumed by subsequent reaction cannot be discounted.

Although Scheme10 accounts, formally at least, for the observed formation of chlorobenzene, bromobenzene and phenyl acetate, this mechanism would not account for the marked differences in the K^{Br}_{Cl} abstraction ratio shown by N-nitrosoacetanilide and

phenylazotriphenylmethane. The clear difference lies in the intermediacy of diazonium salts in the reactions of the former.

Several mechanisms can be suggested for the formation of benzenediazonium chloride in the reaction of N-nitrosoacetanilide with bromotrichloromethane. One possible mechanism is via a modification of Scheme 10, where dissociation of trichloromethyl phenyldiazotate would lead to formation of benzenediazonium chloride along with an equivalent amount of phosgene. Thomson [66], however, has shown that the

$$Ph\text{-}N{=}N\text{-}OCCl_3 \longrightarrow PhN_2^+ \; Cl^- + COCl_2$$

decomposition of N-nitrosoacetanilide in carbon tetrachloride did not give phosgene. Although in both carbon tetrachloride and bromotrichloromethane, the faint odour of phosgene was evident, it was not present in quantity. (The decomposition of 1g of N-nitrosoacetanilide in bromotrichloromethane to give benzenediazonium chloride via this mechanism would require formation of ca. 75 ml of phosgene at 20°).

A second possible mechanism for the formation of benzenediazonium chloride is via ionic attack on bromotrichloromethane. DeTar[56] has shown that when hydrogen chloride was passed into a solution of N-nitrosoacetanilide in benzene, benzenediazonium

chloride was precipitated. If the formation of benzenediazonium chloride in the decomposition of

$$H^+ Cl^- + PhN_2^+ OAc^- \longrightarrow PhN_2^+ Cl^- + AcOH$$

N-nitrosoacetanilide in bromotrichloromethane is via reaction of this type, the necessary chloride ions could arise as a result of ionic attack on bromotrichloromethane, e.g.,

$$PhN_2O^- + BrCCl_3 \longrightarrow PhN_2OBr + CCl_3^-$$

$$CCl_3^- \longrightarrow Cl^- + CCl_2:$$

$$Cl^- + PhN_2^+ OAc^- \longrightarrow PhN_2^+ Cl^- + OAc^-$$

Attack of benzenediazotate ions on bromotrichloromethane would lead to iormation of trichloromethyl ions which could dissociate to give chloride ions and dichlorocarbene. Although the formation of an equivalent amount of dichlorocarbene would be required by the above scheme, exhaustive attempts to trap this species with cyclohexene and the efficient carbene trap α-methylstyrene failed to give any adduct. Consumption of the carbene traps in these experiments by radical induced chain reactions was prevented by the addition to the reaction mixture of a stable free radical or other radical scavenger. Those employed were "galvinoxyl", 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxide and t-butylcatechol. However, the possibility of subsequent reaction of

the carbene, if formed, with some ionic species cannot be discounted. Other evidence in favour of formation of the diazonium halide by the latter-mentioned mechanism will be presented below (p. 194).

Cationic attack by the benzenediazonium cation on bromotrichloromethane would also lead to the formation of benzenediazonium chloride.

$$PhN_2^+ + BrCCl_3 \longrightarrow PhN_2^+\,Cl^- + BrCCl_2^+$$

$$BrCCl_2^+ \xrightarrow{OAc^-} BrCCl_2OAc$$

This would, however, involve the formation of the unstable ester bromodichloromethyl acetate. In similar reactions with methylene chloride and tetrachloroethane, the stable esters chloromethyl acetate and α,β,β,-trichloroethyl acetate would be expected; these, however, were not detected. It will be postulated later that the reaction of N-nitrosoacetanilide with hydrogen containing halogenomethanes may involve rather less diazonium salt participation, so the absence of these esters need not be taken as direct evidence against the above mechanism.

Another possible mechansim leading to the formation of benzenediazonium chloride is via a

one electron transfer process, where reaction between the trichloromethyl radical and the diazotate anion gives the diazotate radical and the trichloromethyl anion (Scheme 11):

$$Ph\cdot + BrCCl_3 \longrightarrow PhBr + CCl_3\cdot$$

$$Ph\text{-}N{=}N\text{-}O\text{-}N{=}N\text{-}Ph$$

(from Scheme 10)

$$\downarrow\uparrow$$

$$PhN_2O^- + PhN_2^+$$

$$CCl_3\cdot \longrightarrow PhN_2^+\ Cl^- + CCl_2:$$

$$CCl_3\cdot \longrightarrow PhN_2O\cdot + CCl_3^-$$

Sceme 11.

If this were the correct mechanism, the formation of benzenediazonium chloride would be prevented by the presence of the stable free radicals in solution. However, due to the fact that the stable radicals were held partly in solution and partly precipitated, it was not possible to decide whether the formation of diazonium salt occurred. Again if chlorobenzene were formed only by some free radical process, its formation would be prevented by the presence of stable free radicals, but chlorobenzene was a product of the reaction in all trapping experiments involv-

ing the reaction of N-nitrosoacetanilide with bromotrichloromethane.

The reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane has also been studied. Reaction at 15° gave a mixture of chlorobenzene, bromobenzene, phenyl acetate, 1,2,3,4-tetraphenylnaphthalene and the mixture of diazonium salts as before. In this

$$PhN(NO)Ac \xrightarrow[\text{trap } 15^\circ]{BrCCl_3} \left.\begin{array}{l} PhCl + PhBr + PhOAc + PhN_2^+\ Cl^- \\ \quad 4.2\% \quad 28.0\% \quad 17.0\% \quad PhN_2^+\ OAc^- \end{array}\right\} + \underset{14\%}{1,2,3,4\text{-tetraphenylnaphthalene}}$$

reaction it was not possible to use the diazonium salts formed in the reaction at 15° for the subsequent decomposition, so a parallel experiment was employed to produce the mixture of diazonium salts for the subsequent decomposition in bromotrichloromethane in the presence of 2,3,4,5-tetraphenylcyclopentadienone at 50°. The combined results are shown in Table 23. It is noteworthy that in a control experiment, benzenediazonium chloride was shown to decompose in bromotrichloromethane in the presence of 2,3,4,5-tetraphenylcyclopentadienone to give chlorobenzene, bromobenzene and 1,2,3,4-tetraphenylnaphthalene.

$$PhN_2^+ Cl^- \xrightarrow[\text{trap}]{BrCCl_3} PhCl + PhBr$$

37.0% 11.0%

+ 1,2,3,4-tetraphenylnaphthalene

5.4%

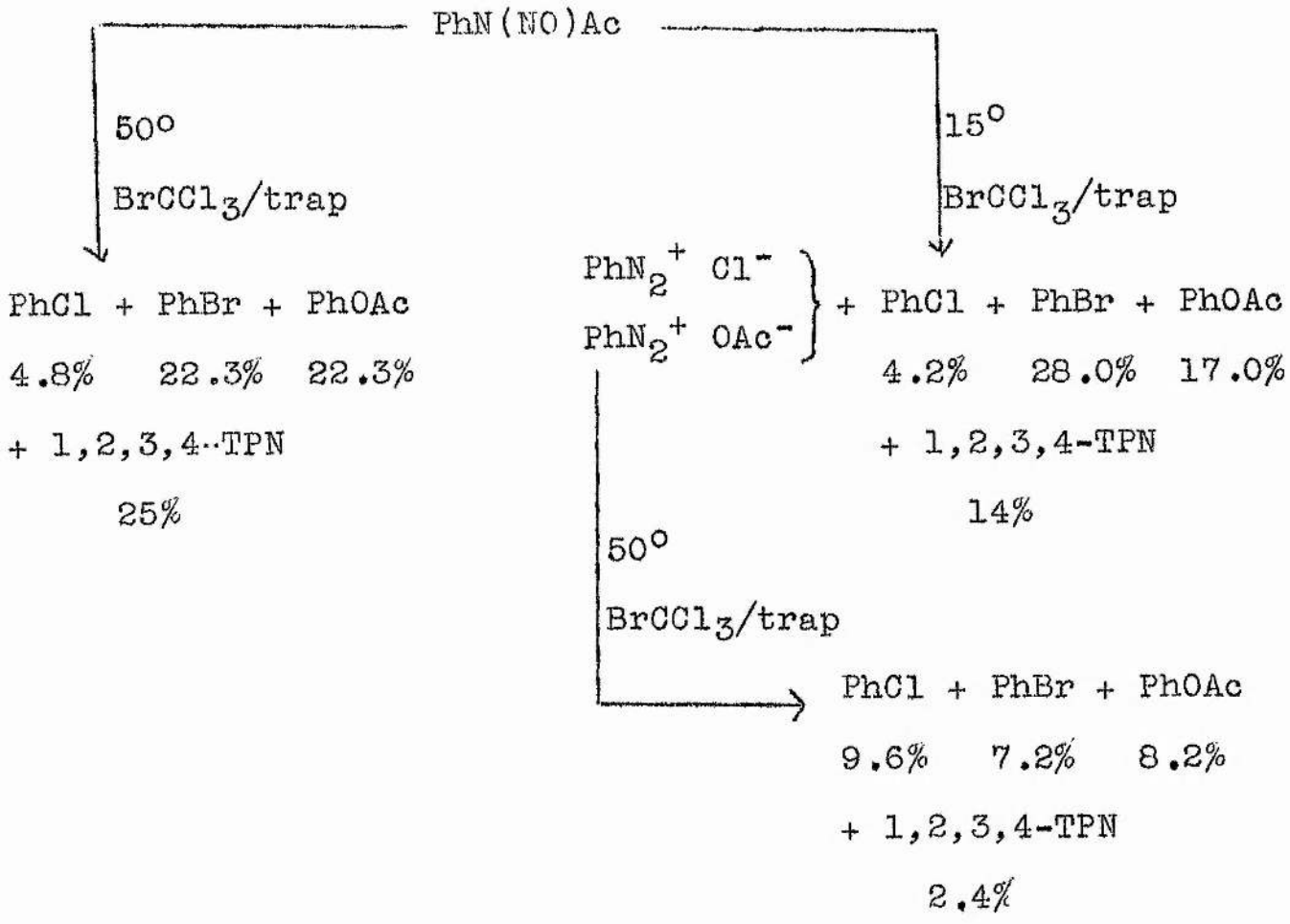
TABLE 23

Reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane

Product	Yield (%)		
	NNA/15°	Diazonium salt/50°	NNA/50°
Chlorobenzene	4.2	9.6	4.8
Bromobenzene	28.0	7.2	22.3
Phenyl acetate	17.0	8.2	22.3
1,2,3,4-TPN	14.0	2.4	25.0
K_{Cl}^{Br}	6.7	2.6	0.75	4.6
Accountance (%)	80.6		75.4

NNA = N-nitrosoacetanilide, 1,2,3,4-TPN = 1,2,3,4-tetraphenylnaphthalene. K_{Cl}^{Br} = moles PhBr/moles PhCl.

A comparison of the abstraction ratios K_{Cl}^{Br} shows again that at 15°, bromobenzene is the major product (K_{Cl}^{Br} = 6.7), but on heating the diazonium salt with fresh bromotrichloromethane and 2,3,4,5-tetraphenylcyclopentadienone at 50° the ratio is K_{Cl}^{Br} = 0.75. Overall abstraction ratios are 2.6



for the stepwise reaction, and 4.6 for the reaction of N-nitrosoacetanilide with 2,3,4,5-tetraphenylcyclopentadienone in bromotrichloromethane at 50°. These results, although showing a little more variance than those obtained in the absence of the trapping agent, are nevertheless consistent with formation of benzenediazonium chloride and benzenediazonium acetate in the reaction at 15°.

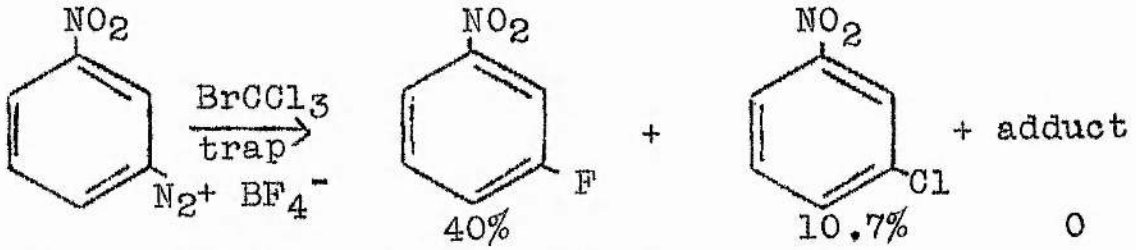
The mechanism of formation of the aryne adduct via possible benzyne or benzynoid intermediates has been discussed above. The remarkable formation of

1,2,3,4-tetraphenylnaphthalene from benzenediazonium chloride led to trapping experiments in which other diazonium salts, both halides and fluoroborates, were allowed to decompose in the presence of 2,3,4,5-tetraphenylcyclopentadienone in the hope of isolating the aryne adduct. (See Tables 8 and 9 pp. 104-6). In all these experiments, only the diazonium halides afforded 1,2,3,4-tetraphenylnaphthalene. The

$$PhN_2^+\ Br^- \xrightarrow[\text{trap}]{BrCCl_3} \underset{3.3\%}{PhCl} + \underset{68.2\%}{PhBr} + \underset{0.9\%}{1,2,3,4\text{-TPN}}$$

thermal decomposition of diazonium fluoroborates yielded the aryl fluorcbenzene as the major product.

e.g.,



B <u>Reactions of acylarylnitrosamines with other halogenomethanes</u>

The reactions of acylarylnitrosamines with other halogenomethanes gave results which again differed from those from similar reactions of the free radical source phenylazotriphenylmethane. Tables 24,25 and 26 show the results obtained with bromoform, methylene bromide and methylene chloride.

TABLE 24

Reaction of N-nitrosoacetanilide and phenylazotriphenylmethane with bromoform

Product	Yield (%)	
	NNA	PAT
Benzene	1.8(2.1)	4.1(3.8)
Bromobenzene	39.0(43.0)	63.0(52.0)
Phenyl acetate	10.0(10.0)	-
Methylene bromide	1.7(1.7)	31.0(23.0)
K_H^{Br}	21.6(20.3)	15.4(13.7)

TABLE 25

Reaction of N-nitrosoacetanilide and phenylazotriphenylmethane with methylene bromide

Product	Yield (%)	
	NNA	PAT
Benzene	10.6(10.5)	24.0(23,0)
Bromobenzene	45.2(45.3)	24.0(19.0)
Phenyl acetate	6.7(7.2)	-
Bromoform	5.4(5.2)	0
K_H^{Br}	4.3(4.3)	1.0(0.8)

TABLE 26

Reaction of N-nitrosoacetanilide and phenylazotriphenylmethane with methylene chloride

Product	Yield (%)	
	NNA	PAT
Benzene	18.0(21.4)	72.4
Chlorobenzene	19.7(23.6)	0
Phenyl acetate	20.0(16.2)	-
K_H^{Cl}	1.1(1.1)	0

It was thought that the reaction of N-nitrosoacetanilide in these solvents might be via a scheme involving diazonium salts, analogous to the reaction with bromotrichloromethane. However, on filtering concentrated solutions of N-nitrosoacetanilide in methylene bromide and bromoform, small quantities only of benzenediazonium bromide were obtained. Similarly in methylene chloride, only a small quantity of benzenediazonium chloride was abtained. It is possible, however, that in the case of formation of benzenediazonium bromide, the bulk of the salt is held in solution, for the diazonium bromide is known to be more soluble than the diazonium chloride.

The abstraction ratios K_H^{Br} and K_H^{Cl} show con-

siderable variation between N-nitrosoacetanilide and phenylazotriphenylmethane. Thus for bromoform, K_H^{Br} is 21.6 and 15.4 respectively, for methylene bromide 4.3 and 1.0, and for methylene chloride 1.1 and 0 respectively.

Further experiments showed that on varying the para-substituent in the anilino moiety of the acylarylnitrosamines, the values obtained for K_H^{Br} from decomposition in methylene bromide varied from 6.0 in the case of an electron withdrawing substituent (COOEt), to 3.1 in the case of an electron releasing substituent (OMe). Variation of the size of the acyl group, however, made little difference to the ratio (Table 27).

These results would seem to favour a mechanism involving abstraction by an ionic species, and the observation that formation of the aryl bromide was preferred when an electron withdrawing substituent (COOEt, NO_2) was present, would indicate the stabilisation of a negatively charged species as the aryl bromide precursor, possibly the diazotate anion (Scheme 12).

$$Ar\text{-}N{=}N\text{-}O^- + CH_2Br_2 \longrightarrow Ar\text{-}N{=}N\text{-}OH + CHBr_2^-$$

$$ArN_2^+ + CHBr_2^- \longrightarrow ArN_2^+\ Br^- + CHBr:$$

(from $ArN_2^+\ OAc^-$) $\qquad\qquad\qquad\qquad\qquad\qquad$ $\downarrow$

$$ArBr + N_2$$

Scheme 12.

TABLE 27

Reaction of acylarylnitrosamines with methylene bromide

$$R' C_6H_4N(NO)COR'' \xrightarrow{CH_2Br_2} R'C_6H_4Br + R'C_6H_5 + R'C_6H_5OCOR''$$

R'	R''	K_H^{Br}
p-COOEt	CH_3	6.0
p-NO_2	CH_3	5.2
p-H	CH_3	4.3
p-OMe	CH_3	3.1
Ph	H	5.1
Ph	C_2H_5	5.5
Ph	$C_3H_7^i$	5.5

Alternatively, reaction could occur via a one electron transfer process similar to that proposed for the reaction of N-nitrosoacetanilide with bromotrichloromethane (Scheme 13):

$$Ar\cdot + CH_2Br_2 \longrightarrow ArH + CHBr_2\cdot$$

(from Schemes 3 and 4)

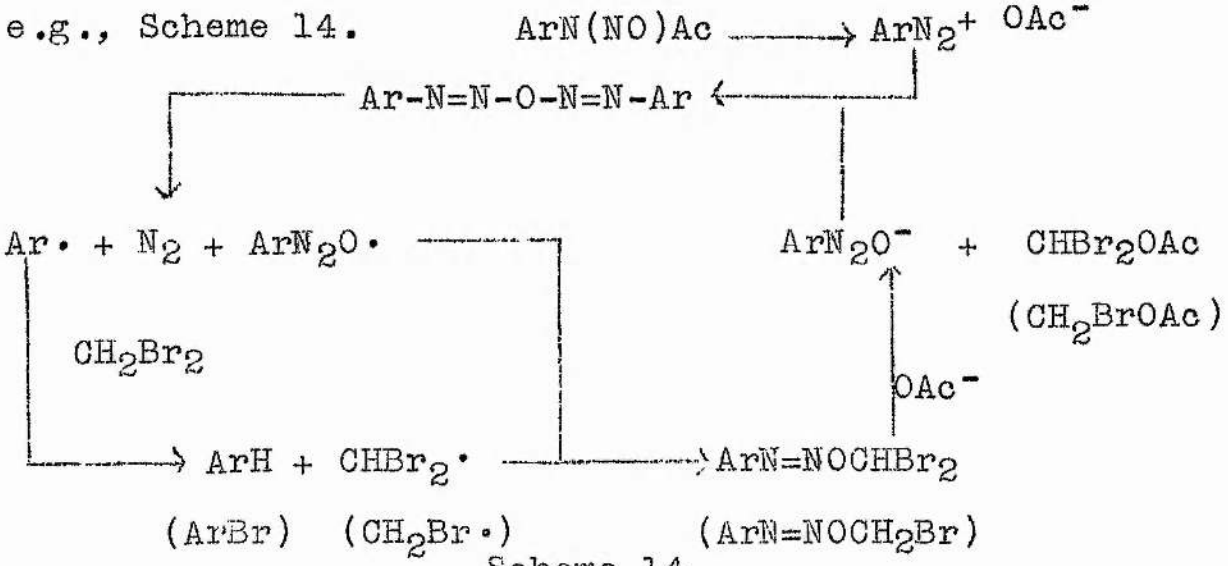
$$CHBr_2\cdot + Ar\text{-}N{=}N\text{-}O^- \longrightarrow Ar\text{-}N{=}N\text{-}O\cdot + CHBr_2^-$$

$$CHBr_2^- \xrightarrow{ArN_2^+} ArBr + N_2 + CHBr:$$

Scheme 13.

As before, the more soluble diazonium bromide would be held in solution, not precipitated like the chloride.

In methylene bromide and bromoform, there are also hydrogen abstraction products to account for. Since an analogous ionic mechanism is less likely, the mechanism of formation of hydrogen abstraction products would appear to be via a free radical scheme, e.g., Scheme 14.



Scheme 14.

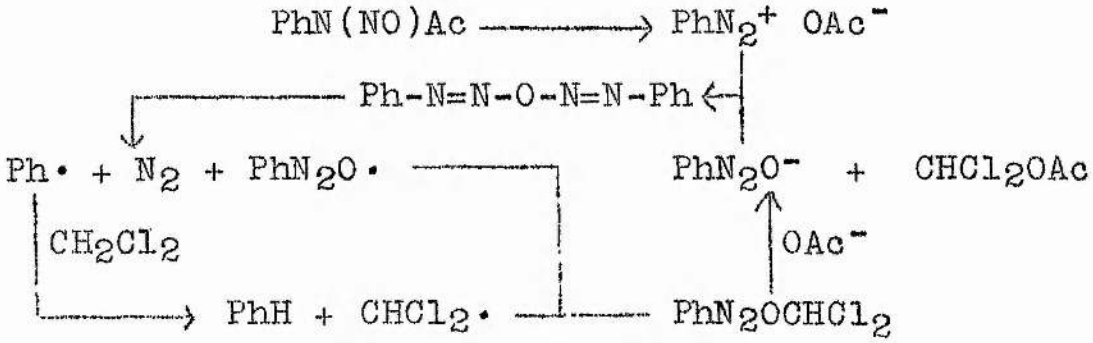
A similar scheme can be written for reaction in bromoform. Although both hydrogen and bromine abstraction products are possible via this scheme, if this were the only mechanism operative, then the K_H^{Br} abstraction ratio would be expected to be the same as that of a similar reaction with phenylazotriphenylmethane. The fact that it is not must imply that there is more than one mechanism operative,

viz., formation of the aryl bromide via the intermediacy of the aryldiazonium bromide.

The reaction of N-nitrosoacetanilide with methylene chloride has been shown to give chlorobenzene (19.7%), benzene (18.0%) and phenyl acetate (20.0%), while that of phenylazotriphenylmethane gave only benzene (72.4%). (Table 26, p. 193). As for reaction in methylene bromide and bromoform, formation of benzene would be best explained by a free radical scheme. Formation of chlorobenzene in the reaction of N-nitrosoacetanilide with methylene chloride is probably via decomposition of the intermediate diazonium salt, since the decomposition of phenylazotriphenylmethane in methylene bromide afforded no chlorobenzene.

$$PhN(NO)Ac \xrightarrow[CH_2Cl_2]{\text{several stages}} PhN_2^+\ Cl^- \longrightarrow PhCl + N_2$$

The free radical mechanism for the formation of benzene in the reaction of N-nitrosoacetanilide with methylene chloride would then be (Scheme 15):



Scheme 15.

This mechanism must be questioned on the grounds that the ester dichloromethyl acetate was not observed, although the possibility that it is consumed by subsequent reaction cannot be ruled out.

Although both free radical and ionic mechanisms have been proposed to explain the reactions of N-nitrosoacetanilide with bromoform, methylene bromide and methylene chloride, it is not possible to state that one mechanism alone operates. This must be so since first, a free radical mechanism is required to explain formation of hydrogen abstraction products, and second, an ionic or partly ionic mechanism is required to explain the formation of diazonium halides.

C The anomalous reaction of p-nitro-N-nitrosoacetanilide with halogenomethanes

The reaction of p-nitro-N-nitrosoacetanilide with bromotrichloromethane and methylene bromide has been shown to give, in addition to halogen and hydrogen abstraction products, a number of rearranged products (Table 28). Reaction of p-nitrophenylazotriphenylmethane, however, gave only the products predicted for a free radical reaction (Table 29).

Hantzsch and Smythe [162] have shown that while o-, and p-bromobenzenediazonium chlorides rearranged to the o-, and p-chlorobenzenediazonium bromides, no such rearrangement occurred with the meta isomer

TABLE 28

Reactions of p-nitro-N-nitrosoacetanilide with halogenomethanes

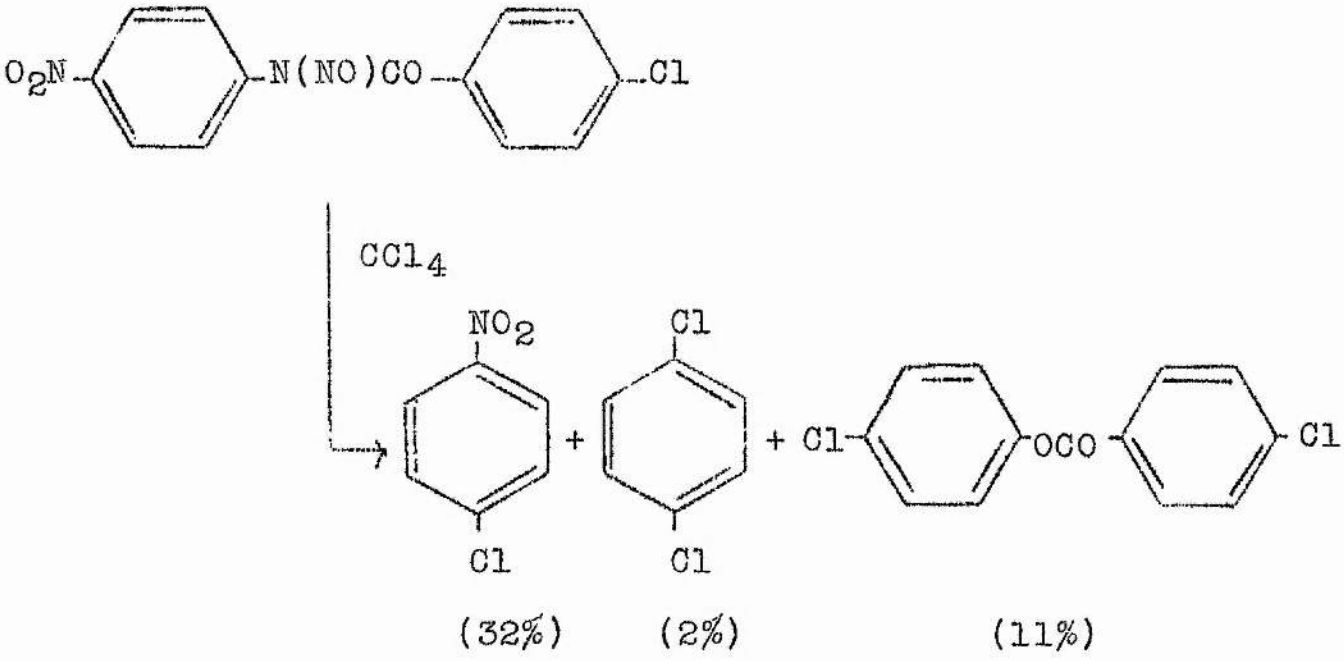
Product	Yield (%)	
	$BrCCl_3$	CH_2Br_2
p-Dichlorobenzene	0.8	-
p-Bromochlorobenzene	2.5	-
p-Chlorophenyl acetate	2.0	-
p-Bromophenyl acetate	4.0	2.9
p-Nitrochlorobenzene	8.0	-
p-Nitrobromobenzene	31.0	43.0
p-Nitrophenyl acetate	3.4	0
Nitrobenzene	-	8.3
Phenyl acetate	-	0.9

TABLE 29

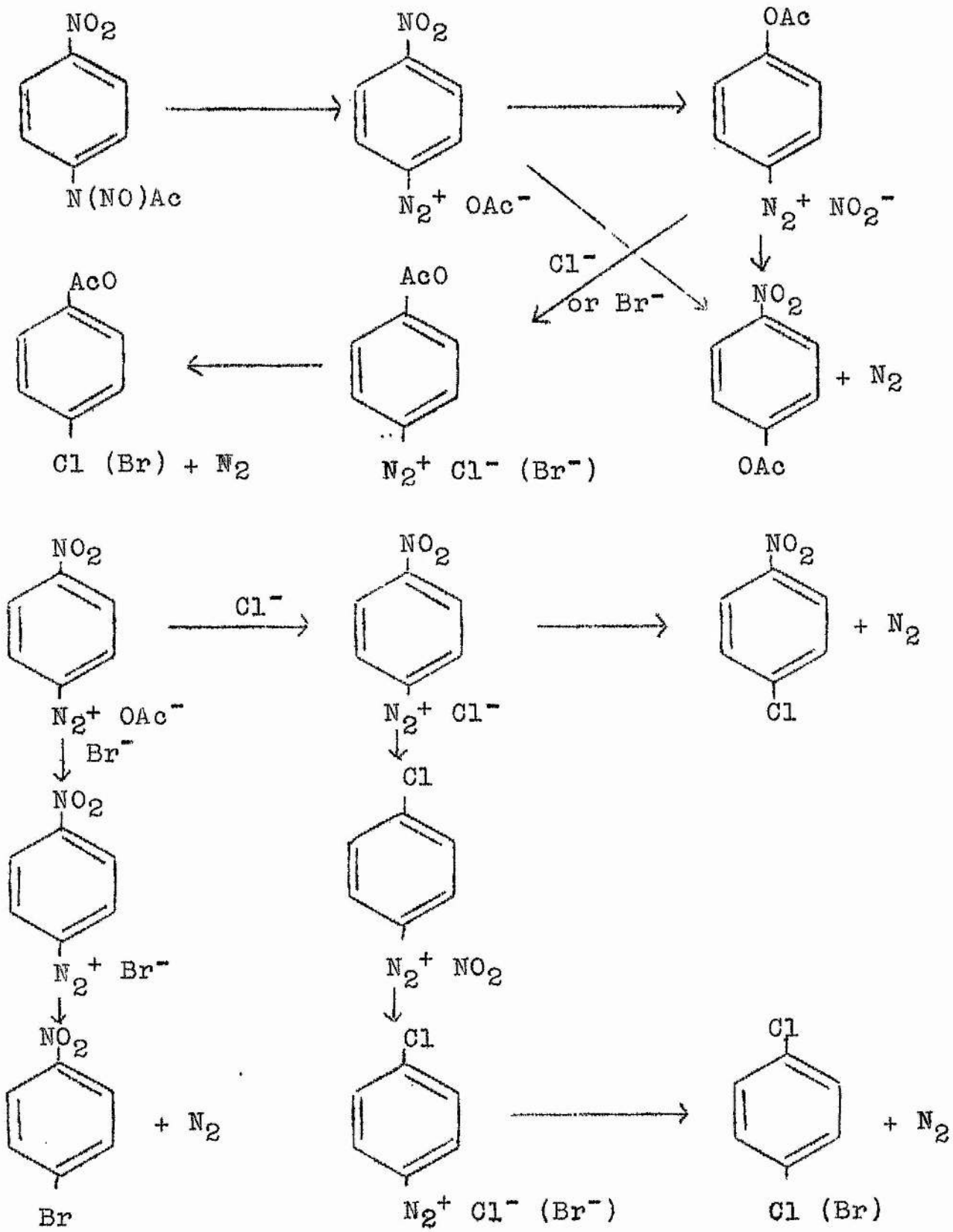
Reaction of p-nitrophenylazotriphenylmethane with bromotrichloromethane

Product	Yield (%)
p- Nitrobromobenzene	69.0
p-Nitrochlorobenzene	0

Suchitsky [59,60,61] has shown that acetate can displace fluoride in the decomposition of o-, and p-fluoro-N-nitrosoacetanilides in benzene, leading to the formation of 4-acetoxybiphenyl. (See Introduction p. 18). Analogous displacement of nitro by acetate is also possible, for Thomson [66] has shown that in the decomposition of 4-chloro-4'-nitro-N-nitroso-benzanilide in carbon tetrachloride, p-dichloro-benzene and 4-chlorophenyl 4-chlorobenzoate were formed, in addition to the expected p-nitrochloro-benzene.



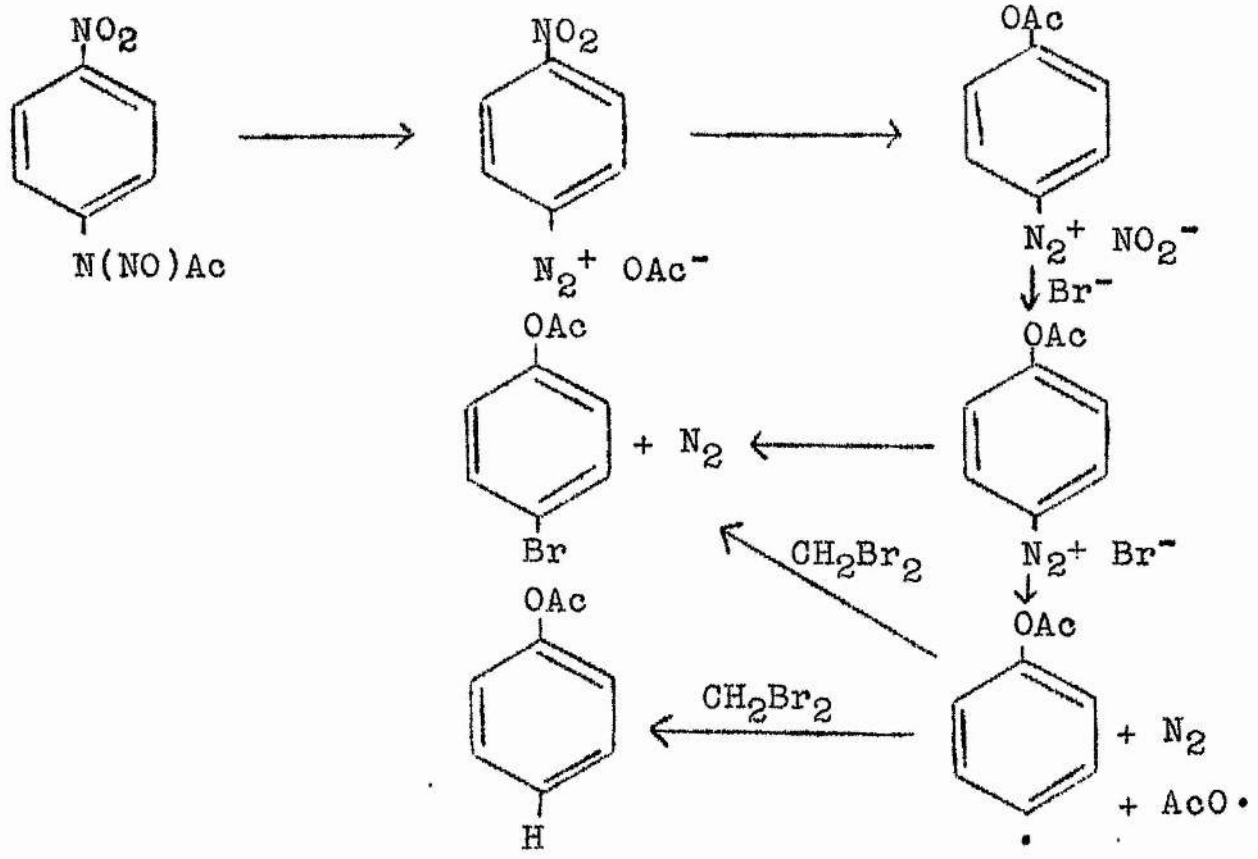
Thus for the reaction of N-nitrosoacetanilide with bromotrichloromethane, we have (Scheme 16):


NO2
N(NO)Ac
N2+ OAc-
OAc
N2+ NO2-
Cl-
or Br-
AcO
Cl (Br) + N2
N2+ Cl- (Br-)
+ N2
OAc
Cl-
+ N2
N2+ OAc-
Br-
N2+ Cl-
Cl
N2+ Br-
N2+ NO2
+ N2
Br
N2+ Cl- (Br-)
Cl (Br)
+ N2

Scheme 16.

In addition, a scheme similar to Scheme 10 (p. 183) can be written to account for halogen abstraction products via a free radical process.

The reaction of p-nitro-N-nitrosoacetanilide with methylene bromide probably involves rather more free radical participation, since this is necessary, as described for the reaction with methylene bromide of N-nitrosoacetanilide itself, to account for hydrogen abstraction products. Formation of p-bromophenyl acetate, however, must have arisen as a result of rearrangement to p-acetoxybenzenediazonium bromide (Scheme 17):

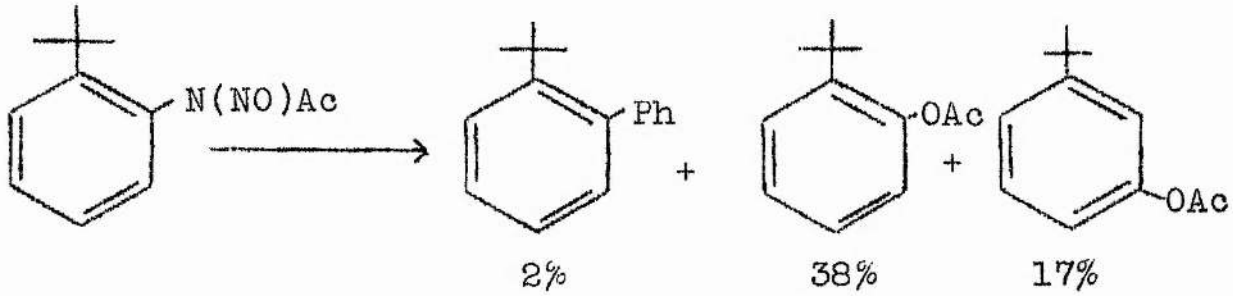


Scheme 17.

The p-acetoxybenzenediazonium bromide, thus formed, could react via intramolecular substitution, or could homolyse to p-acetoxyphenyl radicals which could abstract bromine or hydrogen from the solvent. The latter would account for the observed formation of phenyl acetate (0.9%).

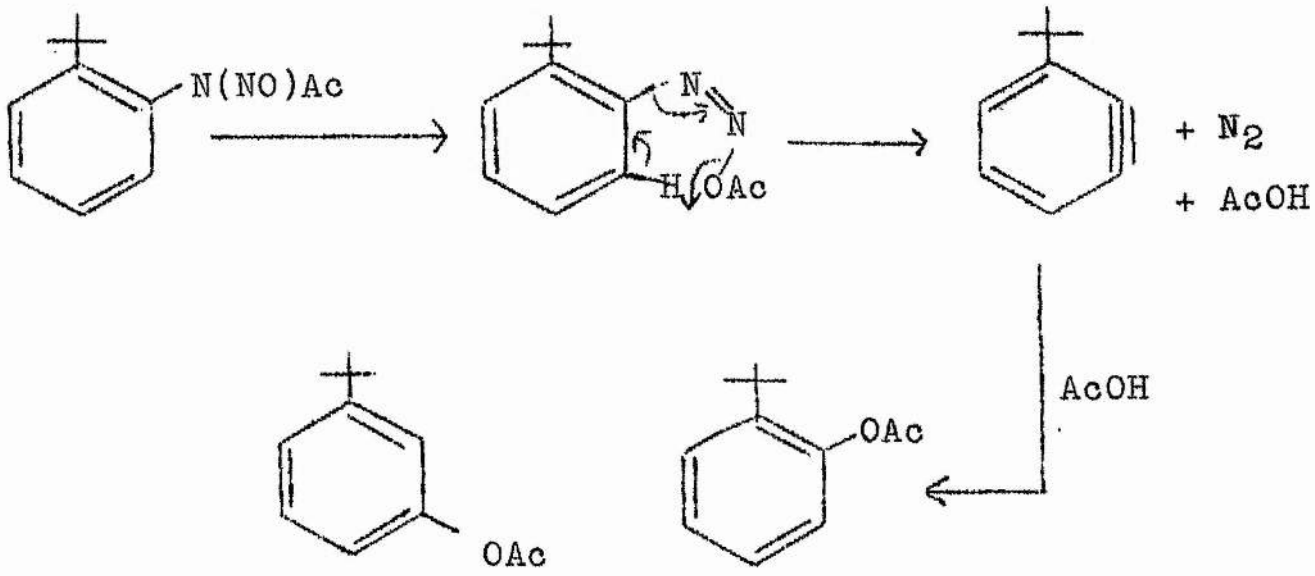
IV The special case of o-t-butyl-N-nitrosoacetanilide

The decomposition of o-t-butyl-N-nitroso-acetanilide in benzene was first studied by Cadogan and Hibbert [79], who showed that whereas the normal decomposition of acylarylnitrosamines in benzene led to the formation of the biaryl (35-70%), that

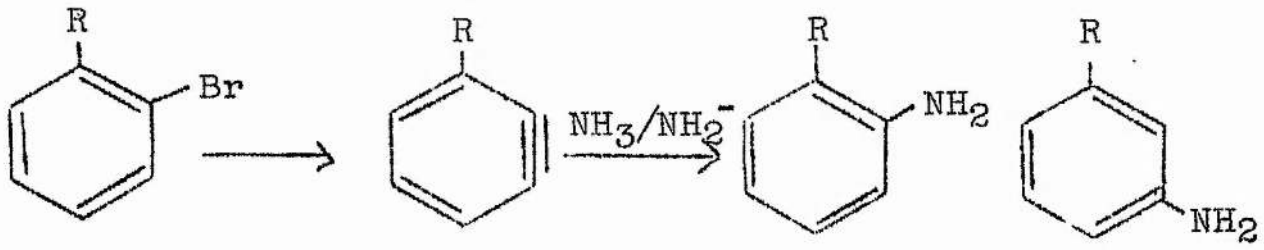


of o-t-butyl-N-nitrosoacetanilide gave only 2% of o-t-butylbiphenyl. The principal products of the reaction were the o-, and m-t-butylphenyl acetates. The formation of the meta-acetate was thought to point to a dehydro aromatic intermediate which subsequently reacted by addition of acetic acid. Cadogan and Hibbert suggested that the bulky ortho-group effected rearrangement to the cis- rather

than the trans diazoacetate, thus facilitating removal of the ortho hydrogen. Later work by Cadogan



et al.[128,163] showed that this was not the whole story, for while addition of amide to 3-methylbenzyne gave a slightly greater amount of o-, rather than m-toluidine, addition of amide to 3-t-butylbenzyne gave almost entirely m-t-butylaniline. It thus seems probable that the formation



R =			
Me	55%	45%
Bu^t	<1%	>99%

(relative yields)

of o-t-butylphenyl acetate in the decomposition of

o-t-butyl-N-nitrosoacetanilide in benzene arises by a non-aryne mechanism. Cadogan et al.[163] have suggested the intermediate formation of a carbonium ion, possibly as part of an ion pair, which leads to formation of the ortho-acetate.

$$ArN(NO)Ac \longrightarrow ArN{=}NOAc \longrightarrow ArN_2^+\ OAc^-$$

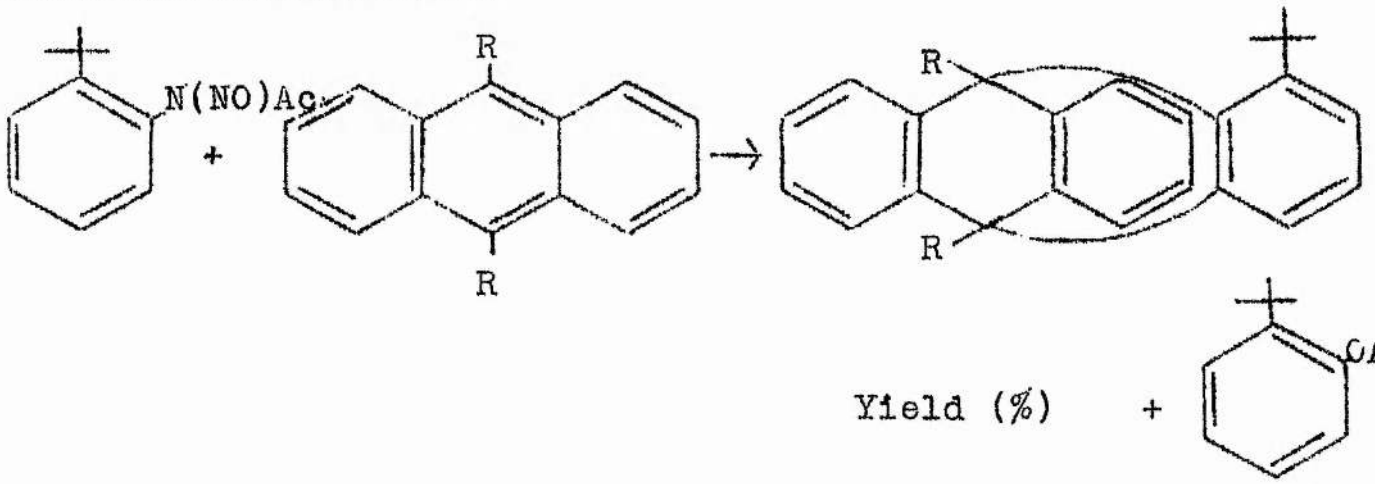
$$\downarrow$$

$$ArOAc \longleftarrow Ar^+\ OAc^- + N_2$$

The results of the present investigation have shown that the postulation of 3-t-butylbenzyne is supported by the isolation of 1-t-butyltriptycene and 1-t-butyl-9,10-dimethoxytriptycene from the reactions of o-t-butyl-N-nitrosoacetanilide with anthracene and 9,10-dimethoxyanthracene in benzene (Table 30).

TABLE 30

Reactions of o-t-butyl-N-nitrosoacetanilide with anthracenes in benzene

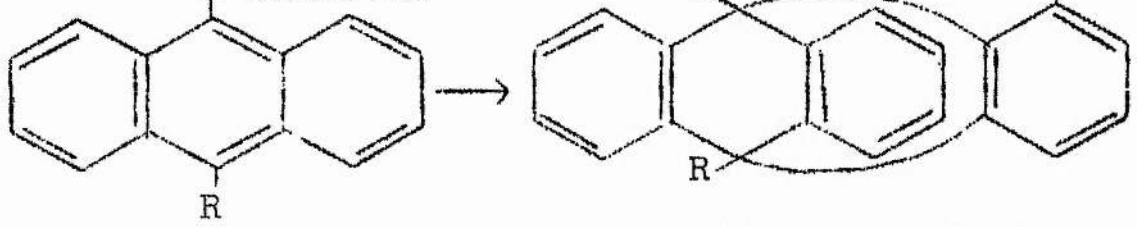


	Yield (%)	+
R = H	19.3	23.0
R = OMe	4.2	15.0

In the former case the yield of adduct was higher than originally found by Cadogan and Hibbert [79]. In both these reactions , formation of the adduct led to a suppression of formation of m-t-butylphenyl acetate. The yields of o-t-butylphenyl acetate, however, were still considerable, (23.0% and 15.0%), consistent with the formation of o-t-butylphenyl acetate via a non-aryne mechanism.

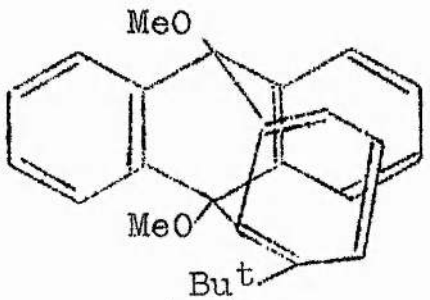
Further evidence for the participation of 3-t-butylbenzyne came from the result of a competition reaction. o-t-Butyl-N-nitrosoacetanilide was allowed to decompose in benzene in the presence of excess of an equimolar mixture of anthracene and 9,10-dimethoxyanthracene. The ratio of the two triptycenes formed was measured and compared to the ratio obtained from a similar reaction using the authentic source of 3-t-butylbenzyne, o-t-butylbromobenzene and potassium t-butoxide. It was found that the two reactions gave identical competition constants. (Table 31). Although the competition constants are the same, it will be seen the the preference of 3-t-butylbenzyne for anthracene rather than 9,10-dimethoxyanthracene is in marked contrast to the reactions of N-nitrosoacetanilide and pentyl nitrite/

TABLE 31

Aryne source + 

Arynophile pair	Solvent	Competition constant o-Bu^t NNA	KOBu^t/ArBr
R = OMe, H	PhH	K^{H}_{OMe} = 13.5 ,	13.3

anthranilic acid with anthracene and 9,10-dimethoxy-anthracene. These reactions led to K^{OMe}_{H} values of 3.2 and 3.1 respectively. This discrepancy is probably due to the greater steric hindrance to addition of 3-t-butylbenzyne to 9,10-dimethoxy-anthracene. This would result in the formation of 1-t-butyltriptycene rather than 1-t-butyl-9,10-dimethoxytriptycene (32).



(32)

The decomposition of o-t-butyl-N-nitroso-acetanilide in halogenated solvents was also

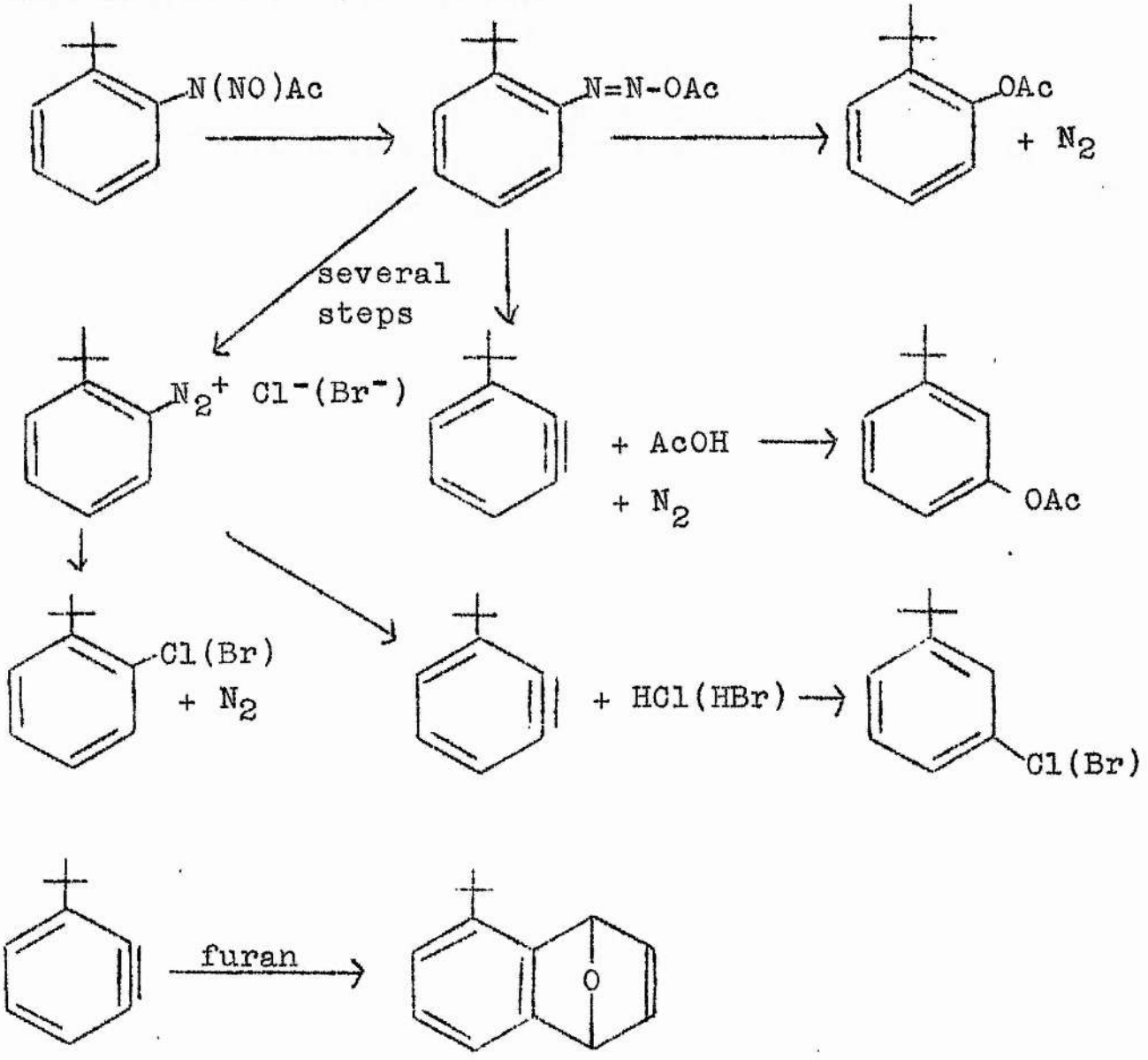
investigated. The results show that in addition to the formation of o-, and m-t-butylphenyl acetates in the decomposition in bromotrichloromethane and methylene bromide, ortho- and meta halogen abstraction products were also observed. When o-t-butyl-N-nitrosoacetanilide was allowed to decompose in bromotrichloromethane in the presence of furan, the aryne adduct 5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide was formed, accompanied by a suppression of formation of the meta halides and acetate.

TABLE 32

Reactions of o-t-butyl-N-nitrosoacetanilide with halogenomethanes

Product	Yield (%)		
	$BrCCl_3$	CH_2Br_2	$BrCCl_3$/furan
t-Butylbenzene	-	2.5	-
o-t-butylchlorobenzene	23.0	-	9.0
m-t-butylchlorobenzene	2.0	-	0
o-t-butylbromobenzene	4.0	14.0	14.0
m-t-butylbromobenzene	0.9	2.5	0
o-t-butylphenyl acetate	45.0	42.0	47.0
m-t-butylphenyl acetate	16.5	21.0	0
5-t-butyl-1,4-dihydronaphthalene-1,4-endoxide			20.0

The reaction of o-t-butyl-N-nitrosoacetanilide with benzene has been seen to proceed via 3-t-butylbenzyne, which can react with acetic acid to form the m-t-butylphenyl acetate. Formation of the o-t-butylphenyl acetate was seen as arising mainly via an intramolecular reaction. A similar mechanism can be written to account for the products in bromotrichloromethane (Scheme 18):



Scheme 18.

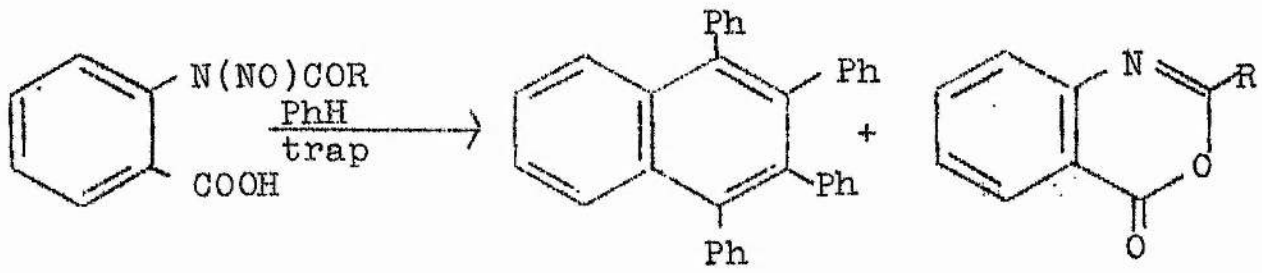
Again a free radical scheme similar to that proposed for N-nitrosoacetanilide (Scheme 10, p. 183) can be written to account for the ortho-t-butyl halides via a free radical mechanism. The reaction of o-t-butyl-N-nitrosoacetanilide with methylene bromide again gave the isomeric acetates and bromides. In this case the amount of hydrogen abstraction from the solvent was slight (2.5% of t-butylbenzene was formed), suggesting slight participation only by a free radical reaction.

Recent e.s.r. work by Cadogan et al.[164] has confirmed this; the signals observed during the decomposition of o-t-butyl-N-nitrosoacetanilide showed poor reproducibility, and no definite conclusions can be reached as to the identity of the chain-carrying radical. It appears therefore, that the main reaction sequence is ionic.

V Other reactions of acylarylnitrosamines

N-nitroso-N-acylanthranilic acids (33) have been shown to decompose in benzene in the presence of 2,3,4,5-tetraphenylcyclopentadienone to give 1,2,3,4-tetraphenylnaphthalene in yields of 6-15%. The major products of the decomposition of these reactive compounds were the cyclised

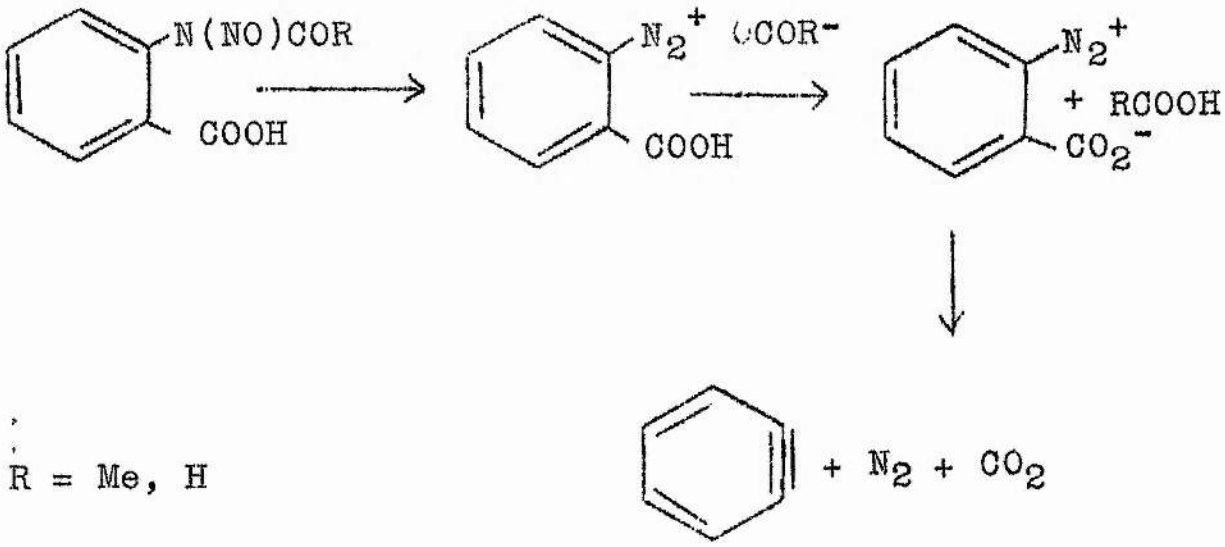
products, the 3,1-benzoxazin-4-ones (34).



(33) (34)

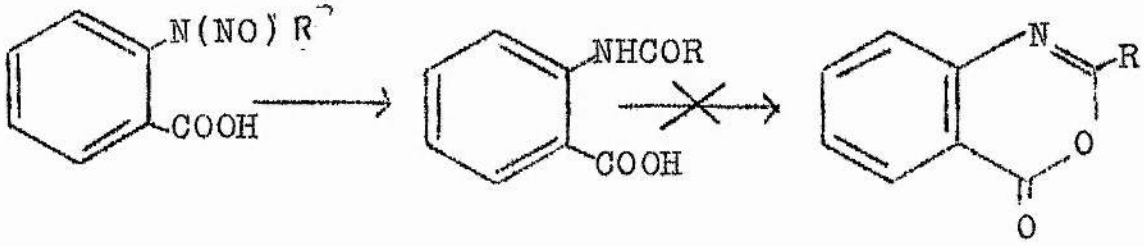
(a) R = Me	6%	16%
(b) R = H	15%	17%

The intermediate leading to the formation of 1,2,3,4-tetraphenylnaphthalene may be benzyne itself in this reaction, since in situ formation of the authentic benzyne source benzenediazonium-2-carboxylate is possible via rearrangement and hydrogen abstraction:



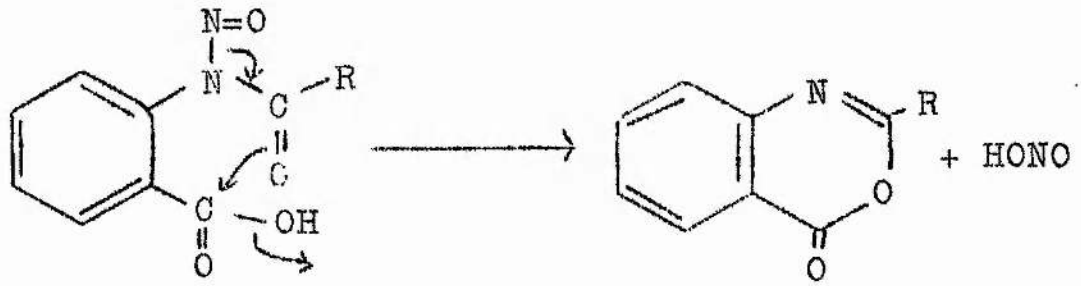
Benzyne thus formed, could undergo cycloaddition in the usual manner.

Formation of 2-methyl-3,1-benzoxazin-4-one and 3,1-benzoxazin-4-one (34 a and b) was shown to be due to the thermal decomposition of the nitrosamide, and not by dehydration of the acylarylamine formed by denitrosation. Control experiments in which the



R = Me, H (34)

acylarylamine was heated in benzene under the conditions of the experiment showed no (34) by g.l.c. Formation of (34) must therefore be via an alternative reaction sequence, e.g.,



R = Me,H (34)

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